

University of Alberta

Role of Oily Bubbles in Enhancing Bitumen Recovery

By

Li Su



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This thesis is dedicated to my husband, Mr. Guozhu Li, and to my daughter,

Sarah Sijing Li, for their love, support and patience.

ABSTRACT

To investigate the mechanisms of how oily bubbles help enhance bitumen flotation recovery from poor processing ores, dynamic contact angle of air/oily bubble on bitumen surface and induction time of bitumen-air/oily bubble attachment in water solution were measured. Oily bubbles showed a marginal effect on contact angle values compared to air bubbles. However, the spreading of oily bubbles on a bitumen surface was found to be much faster than that of air bubbles. The induction time for bubble-bitumen attachment in the process water from poor processing ores was found to be much shorter for oily bubbles than for air bubbles. It is attributed to the lower energy barrier for oily bubbles to attach to bitumen and reduced bitumen viscosity in the vicinity of the bitumen-bubble contact area. The measured induction time correlates well with bitumen flotation recovery.

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TABLE OF CONTENTS

1.0	INTRODUCTION	1
2.0	LITERATURE REVIEW	11
2.1	Flotation and flotation reagents	11
2.2	Oil-aided and oily bubble flotation	18
2.3	Contact angle measurement	22
2.4	Induction time and flotation probability	26
2.4.1	Induction time	26
2.4.2	Flotation probability	32
2.5	Recovering bitumen from oil sands	37
3.0	CONTACT ANGLE MEASUREMENT	49
3.1	Experimental	51
3.1.1	Preparation of bitumen surfaces and process water	51
3.1.2	Experimental techniques	52
3.2	Results and Discussion	55
3.2.1	Contact angles measured in deionized water	55
3.2.1.1	Air bubbles	56
3.2.1.2	Oily bubbles	57
3.2.1.3	Spreading dynamics	58
3.2.2	Effect of water chemistry	61
3.3	Conclusions	63

4.0	INDUCTION TIME MEASUREMENT	64
4.1	Equipment Set-up and experimental method	65
4.1.1	Equipment set-up	65
4.1.2	Experimental method	67
4.2	Results and discussion	71
4.2.1	Effect of aging on induction time measurement	71
4.2.2	Effect of solvent on induction time	73
4.2.3	Effect of water chemistry on induction time	82
4.2.3.1	Air bubbles	82
4.2.3.2	Kerosene-coated bubbles	83
4.3	Conclusions	85
5.0	CORRELATION OF INDUCTION TIME WITH BITUMEN RECOVERY	88
5.1	Conclusion	92
6.0	CONCLUSIONS	93
7.0	RECOMMENDATIONS	96
	REFERENCE	98
	APPENDIX A	106
	APPENDIX A.1: Picture of Experimental Set-up for Induction Time Measurement	107
	APPENDIX A.2: Induction timer material list	108

APPENDIX A.3: Induction Timer Software	109
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APPENDIX A.3.1: Induction Timer Software Control Panel	109
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APPENDIX A.3.2: Induction Timer Software Diagram	110
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LIST OF TABLES

Table 3-1	Water chemistry of process water from different types of ores	52
Table 3-2	Composition of oil sand ores	52
Table 4-1	Pertinent physical properties of the oil and solvents at 20 °C	77

LIST OF FIGURES

Figure 2-1	Contact angle at solid-water-air three phase contact	23
Figure 3-1	Schematic of experimental setup for contact angle measurement	54
Figure 3-2	Initial contact angles of air/oily bubbles on bitumen in deionized water	56
Figure 3-3	Receding contact angles of air/oily bubbles on bitumen in deionized water	58
Figure 3-4	Dynamic contact angle of air/oily bubbles on bitumen surface in deionized water	59
Figure 3-5	Effect of water chemistry on receding contact angle of air bubbles on bitumen in process water	61
Figure 4-1	Schematic of equipment setup for induction time measurement	66
Figure 4-2	Dependence of capillary displacement upon input voltage	67
Figure 4-3	Schematic of the measurement of induction time	69
Figure 4-4	Effect of bitumen aging on induction time of air bubble attaching to bitumen in deionized water	72
Figure 4-5	Effect of oil or solvent film around air bubbles on induction time of bubble attachment to bitumen in process water	75

Figure 4-6	Schematic of interfaces of bitumen/water, air bubble/water and oily bubble/water before bitumen/bubble contact	78
Figure 4-7	Schematic of interfaces of air bubble/bitumen interface and oily bubble/bitumen interface after bitumen/bubble contact	79
Figure 4-8	Energy diagram of bubble-bitumen attachment	80
Figure 4-9	Effect of water chemistry on induction time by using air bubbles	83
Figure 4-10	Comparison of induction time between air bubble and kerosene-coated air bubbles in process water	85
Figure 5-1	Correlations between induction time and bitumen recovery for LHES and Denver flotation cell using air bubble flotation	89
Figure 5-2	Variation of bitumen recovery with time: Effect of kerosene addition to oxidized oil sands ore (reproduced after Vince et al., 2003)	90

1.0 INTRODUCTION

The largest oil sands deposit in the world is located in the province of Alberta, Canada. The total estimate of bitumen in place in Alberta is about 2.5 trillion barrels, of which about 300 million barrels are recoverable through surface mining technologies (Masliyah and Gray, 2003). In 2003, three commercial operations, namely Syncrude Canada Ltd., Suncor Energy Inc., and Albion Sands Energy, collectively produced about 600,000 barrels of oil per day from surface mined oil sands. It is predicted that the production of oil from Alberta's oil sands will represent approximately 60% of Canada's crude oil production by 2010. Since oil sands industry is currently under its second wave of development, by the year of 2030, oil sands industry will be expected to provide about 5 million barrels of oil daily, which will be a significant contribution to Canada's overall energy scenario considering the continual decline of conventional oil reserves (Fairbrother and Flint, 2003; Lord, 2003).

Typical Athabasca oil sand matrix consists of sand grains, clays, water and bitumen. The amount of bitumen in oil sands ranges from 6-16% by weight. The most widely accepted assumption is that there is a thin layer of connate water film (about 10 nm) between each sand grain and the continuum bitumen surrounding the wetted sand grains as shown in a schematic structural model (Takamura, 1985). The connate water film is stabilized between the sand grain and bitumen surfaces by the double

layer repulsive force. This water-wet sand grain characteristic of Athabasca oil sands enables the use of water-based bitumen extraction technology to separate and recover bitumen from sand grains. On the other hand, the sands in other oil sands deposits, such as those in Utah, Venezuela and Trinidad, may not be water-wet. In this case, bitumen cannot be economically recovered through the present water-based extraction processes.

There are two distinct stages during bitumen extraction processes: separation of bitumen from the sand grains, followed by flotation of aerated bitumen. To successfully recover bitumen from oil sands by a water-based process, bitumen aeration is required to create a density difference between bitumen and the continuous aqueous slurry phase, as the density of bitumen is almost the same as that of water. Hence, a key to the success of bitumen separation by flotation is the efficient bitumen-air bubble attachment, which is accomplished in three distinct subprocesses: collision, adhesion, and detachment between bitumen and air bubbles. Studies have shown that ore composition, bitumen viscosity, process temperature, input of mechanical energy and process water chemistry such as pulp pH, divalent cation concentration and release of natural surfactants, are all among the factors controlling the ultimate bitumen recovery from oil sands (Kasongo et al., 2000; Wallwork et al., 2003; Moran et al., 2000; Takamura and Wallace, 1988).

In recent commercial operations using a water-based extraction process, a

recognized challenge is the reduced bitumen recovery when processing ores containing high fines or "weathered" oil sand ores (also called oxidized ores), collectively known as poor processing ores. For such type of ores, bitumen cannot be successfully recovered by the traditional Clark Hot Water Extraction process with a small dosage of sodium hydroxide. In early laboratory loop tests, bitumen recovery from a weathered ore containing approximately 11.5% bitumen by weight was found to be less than 20% (Wallwork et al., 2003), in contrast to a more than 90% bitumen recovery for good processing ores with a similar feed bitumen content. The reason for poor bitumen recovery from the weathered ore was attributed mainly to the deteriorated bitumen-air bubble attachment. The poor flotation behavior of most poor processing ores appears to be caused by the presence of high content of fines or clays and divalent cations. However, the exact reasons are not clear enough. To fully understand poor response of bitumen to flotation and to meet this challenge facing oil sands industry, the mechanisms controlling bitumen-air attachment and hence bitumen flotation recovery need to be established. To accomplish this, the factors affecting bitumen recovery from oil sands need to be further studied. Moreover, since the traditional addition of caustic is normally ineffective for poor processing ores except at a high dosage, major research efforts have been devoted to finding other processing alternatives to meet the challenge of processing poor processing oil sand ores. Alternative processing technologies other than the traditional hot water flotation methods, such as Low Energy Extraction (LEE) process and OSLO oil-aided process, (Logan et al., 1994; Kasperski, 2001) have been proposed and investigated for the

purpose of improving bitumen recovery from poor processing ores and lowering the cost of recovering bitumen from oil sands. The LEE process uses MIBC and kerosene in a 1:2 mix. The amount of MIBC/kerosene added varies depending on ore grade. With the decrease of ore grade, MIBC/kerosene needed will increase in order to keep certain bitumen recovery (Kasperski, 2001). It is recognized that three subprocesses contribute to the control of bitumen recovery: (i) bitumen recession from a sand grain, (ii) bitumen attachment to an air bubble, and (iii) aerated bitumen flotation in a separation vessel (Masliyah and Gray, 2003). Any process or process aid that can enhance the efficiency of any of the above-mentioned three steps will lead to the improvement of bitumen recovery using water-based extraction processes.

Oils are sometimes used as collectors in mineral flotation to enhance recovery, especially when recovering fine particles by flotation. In such separation process, a water-insoluble oil is utilized to either improve the attachment of hydrophobic particles to bubbles (emulsion flotation), to improve flotation of very fine particles by increasing their size (agglomeration flotation), or to increase the size of fine particles to an extent which allows for the separation of the agglomerates by screening (oil agglomeration) (Laskowski, 1992). The early proposed oil flotation showed great potential for improving fine particle recovery (Ralph et al., 1968). However, it is not commercially viable because of the large amount of oils needed for the operation. Later, the technique of using air to promote oil agglomeration for fine coal cleaning was intensively studied (Shen and Wheelock, 2000, 2001). In this

process, a small amount of air was introduced into the coal slurry along with hydrocarbon oil under high shear conditions. By using this technique, an oil film would spread on the bubbles, and the oil-coated bubbles act as carriers to collect hydrophobic coal particles to form compact gas/oil/coal agglomerates. Compared with the case without air addition, not only the amount of oil required was reduced, but also the recovery of fine coal was increased. Inspired by the demonstrated success of using oils as collectors in coal flotation, an innovative idea of using oily bubbles (air bubbles coated by a thin layer of oil or solvent) in oil sands flotation was proposed by Oil Sands Extraction Group at the University of Alberta, Canada. Conventionally, hydrocarbon oil collectors were added directly to the aqueous phase to enhance the mineral hydrophobicity and improve recovery. However, this method may not be economical, considering that a large amount of oil needed may cause undesired synergetic interactions among the flotation reagents and activate gangue particles. Recently, a novel concept of using reactive oily bubbles as a carrier in flotation was proposed by Liu et al. (2002). In addition to the role of agglomerating fine particles, the surface properties of air bubbles coated with a thin layer of oil film can be better controlled. They have demonstrated a much higher contact angle and stronger collecting power by reactive oily bubbles. Moreover, the undesired side effects by adding collectors directly in the aqueous phase can be greatly reduced. Selective flotation by using reactive oily bubble was demonstrated only in single mineral flotation systems with a modified microflotation cell (Liu et al., 2002).

Preliminary research of the oil sands extraction group at University of Alberta had shown that bitumen recovery of poor processing ores could be increased by the addition of kerosene to an air stream feeding to oil sands slurry to an acceptable level comparable to that of good processing ores. It was demonstrated that bitumen flotation recovery increased from ca. 10% to 98% for Suncor's weathered ores and from ca. 20% to 65% for Syncrude's poor processing ores by using kerosene-coated air bubbles instead of air bubbles (Wallwork et al., 2003). Nevertheless, the mechanisms that how oily bubbles help improve bitumen recovery remain to be further investigated.

Flotation is known to be a surface wettability-based separation process. Early studies of wetting phenomena showed that the wetting properties of a solid were dominated by the outermost layer of molecules (Morrow, 1990). Several methods have been developed to determine the wettability of mineral particles, among which are the measurements of contact angle and induction time. Contact angle measurements have been most widely used to determine the wettability of mineral surfaces and provide useful information relevant to mineral flotation processes. Contact angles have also been used in oil sands research to assess the surface hydrophobicity of bitumen in a bitumen flotation system. The measured contact angle in bitumen-air-water system would serve as a marker to indicate how water chemistry affects the hydrophobicity and hence the floatability of bitumen (Kasongo et al., 2000). A good correlation between the measured contact angle and bitumen recovery has been reported: the larger the contact angle, the higher the bitumen recovery (Zhou, 2002;

Kasongo et al., 2000). The knowledge of bitumen-bubble interactions and such surface properties as contact angle and interfacial tension will contribute to optimizing bitumen recovery processes and technologies.

However, contact angle measurements have some limitations due to the thermodynamic nature of contact angle (Yoon and Yordan, 1991; Ye et al., 1989; Lekki and Laskowski, 1971). It is reported that contact angle measurement may not yield sensible response to the changes in a target system or, sometimes, they would even fail to describe the flotation behaviors (Peng, 1996; Ye et al., 1989; Laskowski and Iakra, 1970). Induction time measurement, on the other hand, can provide dynamic information of a system. Induction time as often referred to in mineral flotation is considered to be a more sensitive marker than the conventional contact angle for predicting the floatability of a given system. It has been found in mineral processing industry that the recovery rate of mineral particles is highly dependent on the measured induction time. Specifically, in oil sands flotation, induction time would be a measure of effectiveness of bitumen-air bubble attachment. The induction time is affected by not only the chemistry but also hydrodynamics of the flotation system (Gu et al., 2003).

In this study, both the contact angle and induction time between bitumen and air/oily bubbles were measured in various types of water. Factors affecting induction time measurement were probed in an attempt to understand the role of an oil/solvent

film around air bubbles in bitumen flotation and to support the use of oily bubble flotation for the enhancement of bitumen recovery from poor processing ores. Also, an attempt is made to correlate the measured induction time in process water of different types of oil sand ores with the corresponding bitumen recovery.

With efforts to minimize energy utilization by exploiting low energy oil sands extraction processes, such as oily bubble flotation, the ore characteristics become increasingly critical for efficient bitumen recovery, by exploiting the differences of the bulk and surface properties for the different components in the aqueous phase. In this research, one type of good oil sand ore and two different types of poor processing ores (transition ore and poor ore) were tested in order to study the reasons why poor processing ores respond poorly to bitumen flotation, resulting in a low bitumen recovery. As it is well known, the amount of bitumen in oil sands ranges from 6-16% by weight. A bitumen amount above 10% is considered to be high-grade (rich); a content of 8-10% is considered an average-grade (medium); while a bitumen content of 6-8% is referred to as a low-grade (poor). Low bitumen recovery is often experienced while processing poor processing ores. It should be noted that poor processing ores are often referred to as either high fine ores or weathered (oxidized) ores by industry, mainly to reflect the cause of some poor processing ores being the oxidation of bitumen. However, the characterization of poor processing ores remains a challenge (Wallwork et al., 2003). In this study, transition ore is specifically referred to the ore from Syncrude's Aurora mine, which is found between the upper Esturian

ores and lower marine ores in the Aurora mine pit. This ore contains approximately 9% bitumen and 33% fines (mineral solids less than 44 micron) by weight. Poor processing ore, also provided by Syncrude, contains about 8% of bitumen and 42% of fines by weight.

Following this introduction, a literature review will be given in Chapter 2, which covers the flotation and flotation reagents, oil-aided and oily bubble flotation, contact angle measurement, induction time measurement as well as the previous research work conducted on bitumen flotation.

In Chapter 3, the results of contact angle measurement of bitumen in different types of water and at different temperatures by using both air bubble and oily bubbles will be given with the intention to show that contact angle may not response to the water chemistry changes very well. Comparatively, it is not as sensitive as induction time in terms of reflecting the water chemistry changes and hydrodynamics of the bitumen flotation system.

In Chapter 4, the equipment, methodology and results of induction time measurements of air/oily bubbles attaching to bitumen surface in different types of water will be presented. Factors affecting induction time and the role of the thin oil or solvent film coated on the air bubbles will be investigated.

In Chapter 5, the measured induction time will be compared with bitumen recovery to establish a correlation between two of them. Bitumen recovery curve is obtained with two different flotation devices (Laboratory Hydrotransport Extraction System (LHES) and Denver flotation cell by using air or oily bubbles.

Conclusions will be given in Chapter 6. Some recommendations and suggestions can be found in Chapter 7.

2.0 LITERATURE REVIEW

2.1 Flotation and flotation reagents

Flotation is one of the most important and most widely used processes to separate minerals suspended in aqueous phase from ores by attaching them to gas bubbles. Its applications are being expanded to covering new areas, such as de-inking of recycled paper, emulsified residual oil removal from oily waste water, bitumen recovery from oil sands, and metal oxides extraction, etc. (Grattoni et al., 2003; Kasongo et al., 2000; Oliveira et al., 1999; Takamura and Wallace., 1988; Wills, 1988). Froth flotation utilizes the differences in physicochemical surface properties of various mineral particles and the efficiencies of such surface property-based separation processes rely upon the wettability characteristics, i.e., hydrophobicity/hydrophilicity, of the mineral particles. Three elementary steps are involved in bubble-particle attachment for flotation: (1) bubble-particle collision with the formation of a thin film of liquid between the bubble and particle; (2) thinning of the film to the point of rupture; and (3) rupture and receding of the film, giving rise to a stable contact between the bubble and the particle (Nguyen et al., 1997). In flotation practice, flotation reagents are usually used to control the wettability of a particular mineral or to increase the differences in the surface properties among the minerals in the flotation pulp in order for flotation to take place, or to realize selective flotation, thus, to maximize the recovery of the targeted minerals (Wills, 1988; Ranney, 1980). Flotation reagents are commonly classified into five categories: collectors,

depressants, frothers, activators, and modifiers.

According to their surface characteristics, all minerals are classified into two types: polar or non-polar. The surfaces of non-polar group minerals do not easily attach to the water dipoles and therefore are hydrophobic. Such minerals have high natural floatability with contact angle between 60° and 90° . Although it is possible to float them without the addition of chemical agents, it is common practice to add some hydrocarbon oils or frothing agents in order to increase their hydrophobicity. In fine coal flotation, for example, coal particles are often subject to a suitable hydrocarbon oil treatment to enhance their hydrophobicity and to improve fine coal recovery. Minerals with polar groups are subdivided into five different classes depending on the magnitude of polarity. Since the polar surfaces interact strongly with water molecules, these minerals are naturally hydrophilic. Hence, hydrophobicity has to be imparted to their surfaces in order to float them. To achieve this, surfactants, also known as collectors, are added to the pulp during conditioning period and given enough time for them to adsorb onto the target mineral surfaces (Wills, 1988; Crozier, 1992).

Collectors are the most important reagents. They are surface-active organic reagents that adsorb at the surface of the desired mineral and thereby render the mineral hydrophobic so that the stability of the hydrated layer separating the mineral surface from the air bubble can be reduced to such a level that air bubble can attach to

the mineral surface (Wills, 1988). Some collectors are non-ionizing compounds that are practically insoluble, while other collector molecules are ionizing compounds with asymmetric structure, which contains a non-polar hydrocarbon group and a polar group. The non-polar hydrocarbon radical has pronounced water-repellent properties, while the polar group reacts with water. There are anionic and cationic ionizing collectors depending on the charge of the ionized head group. Anionic collectors, classified into oxyhydrl type and sulphhydrl type, are the most widely used ones in mineral floatation. Carboxylates, which are also known as fatty acids, is among the oxyhydrl collectors. The salts of oleic acid, such as sodium oleate and linoleic acid, are also commonly used. The longer the hydrocarbon chain, the more powerful the water-repulsion produced, but less solubility. Although carboxylates are strong collectors, they have relatively low selectivity. On the other hand, the most widely used sulphhydrl type collectors are not only powerful but also selective. Here, it is worth to mention that a "strong" or "weak" collector does not describe the strength of adhesion between a mineral and a bubble; instead, it is an inverse description of selectivity, or the effect of a particular reagent on the rate of flotation of individual minerals (Crozier, 1992). The most widely used thiol type collectors are the xanthates and dithiophosphates. Most of the time, xanthates are used in their salt forms for sulphide mineral or oxidized mineral flotation. Xanthates are assumed to adsorb on sulphide mineral surfaces due to chemical forces between the polar group and the surface, resulting in insoluble metal xanthates, which are strongly hydrophobic. Cationic collectors are very sensitive to the pH of the medium and most active in

slightly acid solutions and inactive in strongly alkaline and acid media. Amines are the most commonly used cationic collectors, which are relatively weak in collecting power because they are considered to adsorb on the mineral surfaces due to electrostatic attraction between the polar head of the collector and the charges on mineral surfaces.

Non-ionizing collectors, such as kerosene, fuel oil, coal distillates, etc., are liquid non-polar hydrocarbons that do not dissociate in water. Conventionally, the oily collector is added directly to the aqueous solution and time is allowed for adsorption of collectors on the mineral surfaces during the conditioning period. Normally, when oil is dispersed into fine droplets in an aqueous suspension, the interfacial area between the suspended fine particles, liquid and oil droplets is huge, and the dispersed system tends to reduce it by particle aggregation (Laskowski, 2001). In this way, the size of fine particles can be increased as such that the aggregates become easier to float. At the very beginning, hydrocarbon produced as coke-oven by-products was used as collectors. However, they have been replaced by hydrocarbons produced from crude oil (such as kerosene and heptane) because they contain phenol and other toxic aromatic hydrocarbons.

Normally, only small amount of collectors are used to form a monomolecular layer on the particle surfaces since, with the increased concentration, the cost will be going up and the selectivity will be reduced by floating other minerals. An overdose

of a collector can also reduce the recovery of the valuable minerals because of the development of multi-layer collector on the mineral surfaces, which reduces the proportion of hydrocarbon radicals oriented into the bulk solution, reducing the hydrophobicity of the particles and consequently the floatability (Wills, 1988). Nevertheless, it is not uncommon that more than one collector are added to a floatation system. Methods have been investigated to reduce the amount of collector consumptions. Through experiments, it has been shown that increasing the salt concentration will consequently reduce the amount of collectors needed and also increase floatation recovery. The increase in recovery appeared due to compression of the electrical double layer surrounding the individual coal particles and oil droplets. A novel concept of using reactive oily bubbles (bubbles covered by a thin layer of oil) containing oil-soluble collectors as carriers in floatation was recently proposed by Liu et al. (2002). The reactive oily bubble floatation can eliminate the addition of collector directly into the aqueous phase and significantly reduce the amount of collectors needed. Moreover, it avoids undesired synergetic interactions among floatation agents, and minimizes the undesired activation of gangue particles.

In general, collectors adsorb on the mineral particles because of chemical, electrical, or physical attraction between the polar portions and surface sites, leaving their non-polar ends orientated towards the bulk solution, thereby imparting hydrophobicity to the particles. Others also consider the primary function of the collector to be a floatation rate accelerator, or a fine particle agglomerator, in a

particular floatation system (Crozier, 1992).

Frothers are generally heteropolar surface-active organic reagents adsorbing at air-water interfaces. The frother molecules concentrate in the surface layer with the non-polar groups oriented towards the air and the polar groups towards the water. Common frothing agents include alcohols, polyethers, ethylene oxide, and polyglycol ethers (Somasundaran et al., 1988). When surface-active molecules react with water, the water dipoles combine readily with the polar groups and hydrate them, but there is practically no reaction with the non-polar hydrocarbon group, thus the non-polar group is forced toward the air phase. The main role of frothing action is to reduce the air-water surface tension, thus stabilizing air bubbles. Frothers are chemically similar to nonionic collectors in many aspects. On the other hand, many collectors, such as the oleates, in fact, are also powerful frothers. They are too powerful to be efficient frothers because the froths produced will be too stable to be further processed in the following steps (Wills, 1988; Crozier, 1992). In oil sands industry, it is generally considered that the surfactants released from oil sands act as frothers to stabilize air bubbles and ensure that a sufficient number of air bubbles are generated during bitumen flotation process.

Depressants are used to increase the selectivity of flotation by rendering certain minerals hydrophilic and, thus, prevent their flotation. They prevent the adsorption of collectors at the mineral/water interface or prevent the attachment of

bubbles to the mineral surface. Sodium sulfide and cyanide salts are commonly used as depressants in the selective flotation of base metal sulphides.

Regulators, including activators and modifiers, are used to intensify or reduce the water-repellent effect of a collector on the mineral surface, thus make the collector act more selectively towards certain minerals. Activators are generally soluble salts that ionize in solution, and they will alter the chemical nature of mineral surfaces to cause the adsorption of a collector to take place. In flotation, sometimes various inorganic or organic compounds are used as modifiers to modulate the flotation environment by regulating solution chemistry, or by flocculating or dispersing particles in pulp.

Another important fact to be noted is that the pulp alkalinity plays a very important role in flotation. In industrial practice, selectivity in a complex separation system is dependent on a delicate balance between reagent concentration and pH (Somasundaran, 1976; Ranney, M.W., 1980). Under most circumstances for most collectors, flotation can be stably carried out in an alkaline medium. Both organic and inorganic reagents are used in mineral processing, but in general the total tonnage and sometimes the total cost of inorganic compounds are greater. The cost on such pH-control chemicals as lime and sulfuric acid is only next to that of fuel and energy consumption in flotation concentrators and leaching operations (Wills, 1988; Crozier, 1992).

2.2 Oil-aided and oily bubble flotation

The increasing need to separate and recover fine coals and other fine particles using flotation has led to extensive research and development of methods for the efficient and economic recovery of fine particles. Fine particles respond poorly to the conventional flotation process because of the significant changes in their surface properties and associated physicochemical and hydrodynamic conditions in fine particle flotation systems. The small mass of fine particles results in low inertia of fine particles and, thus, low collision efficiency of fine particles with flotation air bubbles (Laskowski, 2001; Liu et al., 2002). Because of the same reasons, even after contacting with an air bubble, the fine particle may not have sufficient kinetic energy to rupture the intervening liquid film between the particle and the air bubble. As a result, three-phase contact cannot be established. Oil agglomeration has been found to be one of the most effective methods for fine particle recovery. During this process, oil is dispersed into fine droplets in an aqueous suspension of hydrophobic particles. The hydrophobic solid particles can be agglomerated by oil droplets since oil will preferentially wet the hydrophobic particles (Laskowski, 2001). Oil droplets will attach to hydrophobic particles and when such particles colloid with each other, the oil droplets attached to hydrophobic particles merge and bridge the particles into larger aggregates. Three major factors controlling oil agglomeration are: (i) the solid wettability; (ii) the amount of bridging oil; and (iii) the type and intensity of conditioning (Garcia et al., 1998).

In oil-assisted separation processes, a water-insoluble oil is utilized either to improve the attachment of hydrophobic particles to bubbles by enhancing hydrophobicity of particles (emulsion flotation), to improve flotation of very fine particles by increasing their size (agglomeration flotation), or to increase the size of fine particles to an extent, which allows for the separation of the agglomerates by screening (oil agglomeration) (Laskowski and Yu, 2000; Laskowski, 1992, 2001). However, direct addition of oil into the aqueous phase for flotation at commercial scale is considered uneconomical, and would incur a relatively high operating cost due to a large amount of oils needed for the operation, unless economical oil recovery and recycle can be realized.

To minimize oil consumption and enhance coal cleaning, extensive research of using air to promote oil agglomeration was carried out (Shen and Wheelock, 2000, 2001). In this case, a small amount of air, either entrained, added or supersaturated, was introduced into coal slurry along with the addition of a hydrocarbon oil under high shear conditions. Under favorable conditions, an oil film would spread on the air bubbles and form oil-coated bubbles. Compared with the cases of no air addition, both the separation efficiency and recovery of fine coals were increased, while the amount of oil required for achieving the same efficiency was reduced.

In coal cleaning process, another technology involving the use of oil is characterized by emulsifying the collector-containing oil phase with the addition of

promoters (Laskowski, 1992). Emulsification of an oily collector not only increases the number of oil droplets and therefore aids flotation kinetics, but also reduces the oil-water interfacial tension, thus improves the spreading of collector-containing oil droplets on the target particle surfaces.

Inspired by the successful application of oil-coated bubbles and emulsified oily collectors in coal flotation, a novel concept of reactive oily bubble (bubbles covered by a thin layer of oil containing oil-soluble collectors) was brought up by Liu et al. (2002), and a systematic fundamental study of reactive oily-bubble flotation was carried out. A distinct feature of reactive oily bubbles is the easy control of oil/water interfacial chemistry by dissolving desired type and concentration of water insoluble collectors in the oil phase. This can not only increase collecting power and improve selectivity of flotation, but also significantly reduce the amount of collectors needed. Moreover, the impact of unintentional activation by cross contamination is greatly minimized.

Flotation by oily bubbles has been tested in other areas, such as solvent extraction, water purification, de-inking process, as well as bitumen flotation (Tarkan et al., 2004; Chen et al., 2003; Gomez et al., 2001; Oliveria et al., 1999; Wallwork et al., 2003). It was demonstrated that coating air bubbles with silicone oil by an aerosol technique enhanced flotation deinking ability over clean air bubbles. The use of silicon oil was found to reduce the amount of air required to match plant brightness

gains (Gomez et al., 2001). Tarkan and Finch (2004) utilized the foaming properties of kerosene-based solvent to generate coated bubbles. High aqueous/organic ratios (e.g. 75:1) could be used while phase separation remained excellent. Air-assisted solvent extraction (AASX) showed a potential to treat large volume, low concentration streams such as acid mine drainage.

In oil sands industry, kerosene together with methylisobutyl-carbinol (MIBC) had been utilized while developing non-Clark extraction processes by other six lease owners (OSLO). The OSLO extraction process is a noncaustic method carried out from 30°C to 90°C using a collector (kerosene) and frother (MIBC) in a 2:1 ratio to improve bitumen recovery (Kasperski, 2001). The role of kerosene is to coat the bitumen surfaces to make them more hydrophobic and thus help air attachment. The role of MIBC is to stabilize the produced froth for better collection. The Low Energy Extraction (LEE) process is a low-temperature version of the OSLO process. LEE process is carried out between 5°C and 35°C. It uses significantly more kerosene and MIBC and higher air addition than OSLO process. However, these processes are not commercially viable for oil sands extraction because of economical and environmental concerns. In other research, kerosene was used to reduce bitumen viscosity during pretreatment step while investigating the effect of bitumen viscosity on bitumen recovery with hot water process (Hupka et al., 1983; Hupka and Miller, 1991). It was considered by the researchers working on this project that bitumen viscosity was the most important oil sand property in determining the success of the

bitumen separation.

The use of oily bubbles in oil sands extraction was first brought up and tested by Oil Sands Extraction Group at University of Alberta. It was demonstrated that bitumen recovery increased from ca. 10% to 98% for Suncor's oxidized ores and from ca. 20% to 65% for Syncrude's poor processing ores by using kerosene-coated air bubbles instead of air bubbles (Wallwork et al., 2003). The application of oily bubble flotation in oil sands industry is appealing. However, the mechanisms of how oily bubbles help enhance bitumen recovery from oil sands remains to be investigated, which is the objective of this research.

2.3 Contact angle measurement

Froth flotation is based on the differences in the affinity for water exhibited by different mineral surfaces. To float the targeted particles, a particle must attach itself to an air bubble. Only hydrophobic minerals with nonpolar surfaces can readily attach to air bubbles and float to form froth. However, most mineral surfaces are highly polar, that is, they are hydrophilic and consequently wetted by water. Therefore, they need to be transformed into nonwetted ones by the adsorption of suitable surface-active agents. A classical condition for particle-bubble contact to be possible is that the free energy change, ΔG , during the attachment process is less than 0, i.e.

$$\Delta G < 0$$

(Equation 2-1)

Traditionally, contact angle measurements are used to assess the floatability of minerals. Contact angle, θ , of an air bubble on a solid surface is defined as the angle measured through the liquid phase at the solid-liquid-air three-phase contact line as illustrated in Figure 2-1 and indicated by the equation:

$$\gamma_{SG} - \gamma_{SL} = \gamma_{LG} \cos \theta \quad (\text{Equation 2-2})$$

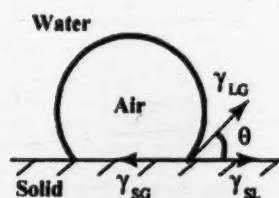


Figure 2-1 Contact angle at solid-water-air three phase contact

By introducing Young's equation, Eq. (2-1) can be expressed as a very useful form

$$\Delta G = \gamma_{LV} (\cos \theta - 1) < 0 \quad (\text{Equation 2-3})$$

Obviously, $\Delta G = 0$ for $\theta = 0^\circ$; If $\Delta G < 0$, then, contact angle θ must be greater than 0 , i.e., $\theta > 0$. This well known equation has been called the thermodynamic criterion of flotation. The larger the contact angle, the higher the affinities for mineral to air bubble than for water, therefore, the greater the floatability of a mineral. Contact angle is considered as the most universal measure of the wettability of surfaces (Morrow, 1990). The critical surface tension concept has offered a unique method to test this thermodynamic flotation criterion. The critical surface tension values obtained by contact angle measurements and flotation tests agree quite well, which represents the best proof of the flotation thermodynamic criterion (Laskowski, 1986).

Also, wettability of liquids on solids plays an important role in the processes of flotation or extraction. For example, in metal extraction, separation of valuable metal oxides from associated rock materials by flotation relies largely on the selective dewetting of metal oxides (Xu and Masliyah, 2001). Three methods are usually used to measure the wettability quantitatively: contact angle, Amott method, and the U.S. Bureau of Mines (USBM) method. Contact angle measurement is the best method used to measure wettability when pure fluids and artificial cores are used (Anderson, 1986).

Similar to mineral processing, in which contact angle measurements have been most often used to determine the wettability of the minerals and oil ores, contact angle measurement was also employed in oil sands research to study the interactions of ionic species with fine solids to better understanding the slime coating problem encountered in the extraction process of oil sands (Zhou et al., 1998). A significant effect of fine solids on contact angle was observed only when the solids were made hydrophobic by adsorbed surfactants. It has been also proved through experiments that bitumen-water-air contact angle correlates well with bitumen recovery: the larger the contact angle, the higher the recovery of bitumen from oil sand ores (Zhou, 2002; Kasongo et al., 2000). The similar correlations between contact angle and targeted mineral recovery have also been demonstrated through experiments in different flotation systems (Liu et al., 2002; Ye and Miller, 1988).

As a conventional method, contact angle measurement has been most widely used to determine the wettability of the mineral surfaces and provide very useful information relevant to flotation processes. However, contact angle measurement has some limitations. It has been found that the contact angle measurements may not yield sensible corresponding information for coal in powder form, yet when used properly, the contact angles can provide valuable insights (Peng, 1996). It is reported that the contact angle measurements would fail to describe the flotation behavior of coal particles which have been shown to be pH dependent (Laskowski and Iakra, 1970). Coal depression by dextrin addition as indicated by flotation recovery can be easily interpreted by the significant increase in induction time, where the contact angle decreases only slightly (Ye and Miller, 1988). In some cases, with other mineral particles, it has been reported that flotation can occur even at zero contact angle (Lai and Smith, 1966). In this regard, further study of the hydrophobic character and flotation behavior of mineral particles by other methods, such as induction time measurement, is of particular importance.

Generally speaking, it has been accepted that contact angle is an equilibrium measure of the hydrophobicity and a purely thermodynamic quantity. Laskowski (1974) cited Klassen and Mokrousov (1963), saying: "Flotation is typically a non-equilibrium process. The phenomena that occur on the surface of particles and bubbles in agitated, aerated mineral pulps, when these particles strike bubbles, are dynamic-non-equilibrium processes which cannot be analyzed based on contact angle

values obtained at equilibrium". In order to get a more general picture of the system, the need to get the kinetic information that can be obtained through the induction time measurement becomes imperative. It was pointed out by Laskowski (1986) that, for a particle to be floatable, not only dewetting of the particle surface has to be thermodynamically favorable, that is, the contact angle $\theta > 0^\circ$, but also the kinetic criteria, the induction time less than the contact time, are also to be satisfied.

2.4 Induction time and flotation probability

2.4.1 Induction time

Of all the subprocesses in flotation, the attachment of mineral particles to air bubbles is the most fundamental requirement for successful flotation. The air bubbles can only attach to the mineral particles if they can displace water from the mineral surface (Wills, 1988). This process involves the thinning and rupture of the wetting film between the colliding particles and air bubbles. Induction time is defined as the minimum time required for the film to drain to a critical thickness and rupture spontaneously to form a stable bubble-particle aggregate (Yoon and Yordan., 1991). It is believed that attachment only occurs when the particle residence time on the bubble surface is longer than the induction time, that is, the particle-bubble contact time is longer than the induction time. Traditionally, a sliding model is used to calculate contact time instead (Sutherland, 1948). Under this model, the contact time is

calculated as the time needed for the particle to slide over the bubble surface under potential flow conditions.

It was proposed by Nguyen et al. (1997) that, for a particle to attach to a bubble, three elementary steps are involved: (i) the intervening liquid film thinning from an original thickness to a critical thickness; (ii) film rupture from the critical thickness to the formation of a nuclei hole with a critical radius, forming a three-phase contact (TPC) line; and (iii) the TPC expansion from the critical radius to a minimum radius (r_m) required for a stable attachment. Therefore, the measured induction time (t) consists, in fact, of the following three components: the time required for film thinning (t_i), film rupture (t_r) and TPC expansion (t_e), that is,

$$t = t_i + t_r + t_e \quad (\text{Equation 2-4})$$

The concept of induction time was first proposed by Sven-Nillson in 1934. Nevertheless, the value that can be provided to us by the measurements of induction time had not been fully recognized until a systematic study was carried out by Eigeles and Volova in 1960. The reason why the study of the floatability of minerals in terms of contact time and induction time received only moderate attention was attributed to both experimental and theoretical difficulties (Ye and Miller., 1988). A lot of research work has been conducted with the intend to find out the factors affecting the measurements of induction time (Gu et al., 2003, 2004; Yoon, 2000; Peng, 1996; Yoon and Yordan, 1991; Ye et al., 1989; Ye and Miller, 1988), understanding the

particle-bubble attachment in flotation (Dai et al., 2000; Yoon and Luttrell., 1989; Luttrell and Yoon, 1988; Fan et al., 1989; Ye and Miller., 1988; Laskowski and Iskra., 1970), setting up models to describe the processes of water film thinning, film rupture, and TPC expansion (Wang et al., 2003; Pugh and Yoon., 1994; Ye and Miller., 1988), and, finally, correlating the measured induction time with the flotation behaviors and flotation recoveries (Peng, 1996; Yoon and Yordan., 1991; Ye and Miller., 1988).

It has been found that induction time is highly dependent on the chemistry of the flotation system and the size of both air bubbles and particles used in the measurement. The main findings from earlier studies are (i) induction time increases linearly with increasing particle size within a definite range (Yoon and Yordan., 1991; Ye and Miller., 1988), attributed to the longer time needed to displace the water film from a larger particle; (ii) the dependence of the measured induction time on particle size is established by particle density and independent of the hydrophobic character of the particles (Ye et al., 1989); (iii) induction time decreases exponentially with increasing temperature (Gu et al., 2003; Fan et al., 1989; Eagles and Volova., 1960); (iv) induction time decreases with increasing electrolyte concentration, attributed to the compression of the electric double layer and the increase of the instability of the intervening wetting film (Gu et al., 2003; Laskowski and Iskra, 1970); (v) induction time decreases with increasing collector concentration (Laskowski and Iskra, 1970; Yoon and Yordan, 1991), attributed to the increase in absorbed collector density on the mineral surface to render the mineral particles more hydrophobic and the wetting

film less stable; (vi) pH also has a great effect on the induction time (Laskowski and Iskra, 1970; Yoon and Yordan., 1991), mainly through affecting adsorption of surfactant and/or the release of surfactants. At a given dodecylamminium hydrochloride concentration, for example, the induction time reaches minimum at pH about 10.5, which corresponds to the formation of ionomolecular surface-active species and the highest flotation recovery (Yoon and Yordan, 1991); and (vi) electrostatic force induced by the electrical charges influences the kinetics of the bubble-particle adhesion process, thus, the induction time. The particle-bubble adhesion process will be accelerated when a repulsive electrostatic force is replaced by an attractive force (Yoon, 2000; Yoon and Mao, 1996; Ye and Miller, 1989). Furthermore, on the basis of some of these findings, Eagles and Volova (1960) calculated the activation energies of bubble-particle attachment using equation

$$t = t_0 \exp (E / kT) \quad (\text{Equation 2-5})$$

where t_0 is a constant; E is the apparent activation energy dependent only on the nature of the mineral and solution chemistry; k is the Boltzman constant; T is the absolute temperature;

In fact, it had long been noticed that induction times obtained by experiments were not only affected by the aforementioned factors, but also greatly dependent on the experimental setup. Although it was reported that induction time is a function of many physical parameters, no detailed experimental information was available until a systematic research was carried out by Gu et al. (2003). Theoretical studies showed

that the induction time measured by moving an air bubble toward and then away from a mineral bed in a liquid is a function of particle density, particle size, air bubble size, the velocity of the air bubble approaching to and retracting from the mineral bed, the initial gap between the air bubble and the particle bed, the viscosity, density and surface tension of the liquid, and the three-phase contact line tension. When studying the effect of physical parameters on induction time measurement using a model system of an air bubble attaching to a silica particle bed, it was found that (i) the higher the extent of air bubble compression, the higher is the pressure applied to the water film, hence, the shorter the induction time is; (ii) the larger the air bubble size, the longer the induction time; (iii) with a fixed retracting velocity of the air bubble, the measured induction time first decreased with increasing approaching velocity of the air bubble, then, leveled off beyond a certain approaching velocity; On the other hand, with fixed approaching velocity of the air bubble, the measured induction time first increased with the increasing retracting velocity of the air bubble, and then, also leveled off. These findings suggest that not only is induction time sensitive to the chemistry change of the system, but also to the set of physical parameters used in induction time measurement. Therefore, it is necessary to choose appropriate physical parameters with the lowest sensitivities for induction time measurements in order to obtain reliable and reproducible data.

It is well recognized that induction time is a function of both the chemistry and hydrodynamics of the system and provides dynamic information of the system. To a

large extent, the relative magnitude of the induction time for different types of particles is a fundamental physicochemical property which determines the flotation behavior of a given particle population. In this regard, induction time is considered to be a better marker for flotation than contact angle, which, on the other hand, is only a thermodynamic quantity. During the investigation of so-called "salt flotation", it was found by Laskowski and Iskra (1970) that the measured induction time and flotation behavior were greatly influenced by the concentration of KCl, while contact angle remained almost unchanged. Induction time measurements were also chosen by Yoon and Yordan (1991) to study the quartz-dodecylamine system because contact angle and surface tension could not successfully describe the dynamic flotation behavior of this system. In studying of the floatability of coals of different rank by using Hallimond-tube through the measurements of both induction time and contact angle, it was noticed that induction time instead of contact angle could be used to describe the floatability of coals as shown by a systematic trend of induction time with respect to floatability of coal. Depression of coal floatability by dextrin addition could be easily interpreted by a significant increase in induction time, where the contact angle decreased only marginally (Hupka et al., 1991; Hupka and Miller, 1983). Selective flotation is in fact achieved by maximizing the difference in induction time for different particle types.

Induction time was recently used to investigate bitumen-air bubble attachment during oil sands extraction process (Gu et al. 2003, 2004; Wang et al., 2003). It is

found that induction time is strongly dependent on temperature and on any factor that affects the interfacial properties such as water chemistry. In this regard, induction time should be a more valuable marker to assess the oil sands flotation process because it is more sensitive than contact angle to the changes in a flotation system.

2.4.2 Flotation probability

It is well known that the thermodynamic criterion of flotation is a net reduction of the free energy during the particle-bubble attachment process, i.e., $\Delta G = \gamma_{LV}(\cos \theta - 1) < 0$. This equation can be interpreted as follows: the more negative the ΔG value, or the larger the contact angle, the greater the probability of flotation. It is clear now that, in order for a particle to be floatable, not only must dewetting of particle surface be thermodynamically favorable, but also other criteria have to be satisfied: (i) a particle must collide with a bubble; (ii) the disjoining film separating the particle and bubble must thin, rupture and recede during the collision; (iii) the particle-bubble aggregate formed must have a sufficient strength to withstand the shearing forces in the flotation cell.

While modeling the flotation behaviors, the process of bubble-particle attachment is usually divided into three subprocesses including collision, adhesion and detachment (Yoon, 2000). The probability of bubble-particle collision and adhesion is derived on the concept that the bubble-particle adhesion can only occur

when the particle-bubble contact time is longer than the induction time. Laskowski (1974) proposed that all of the above criteria could be expressed in terms of the probability of flotation, P , which could be expressed by

$$P = P_c P_a P_s \quad (\text{Equation 2-6})$$

where P_c , P_a and P_s represent, respectively, the probabilities of collision between particles and gas bubbles, adhesion of the bubble to particle, and the formation of a stable bubble-particle aggregate. Later, Yoon et al. (2000) suggested that the complex flotation process could be represented by the equation

$$P = P_c P_a (1 - P_d) \quad (\text{Equation 2-7})$$

where P , P_c and P_a bear the same meaning as defined above, while P_d stands for the probability of detachment. It is recognized that P_c is primarily a function of particle size, bubble size, and microturbulence in a flotation cell; while P_a is connected to the chemistry of the aqueous phase, particle size and bubble size (Yoon and Luttrell, 1989). More importantly, it is dictated by the rupture of the disjoining film between the air bubble and the particle, and thus, it is connected to induction time (Laskowski, 1974; Luttrell and Yoon, 1988; Yoon and Luttrell, 1989). P_s , on the other hand, can be taken as a function of contact angle, the size of the bubble, and also the size and density of the particle. Among all the aforementioned three elementary subprocesses, the hydrodynamics of particle-bubble collision has been most extensively studied, and the results are very useful for the design and scale-up of flotation cells (Yoon, 2000).

At the beginning of flotation history, two different mechanisms were proposed

for the interaction of particles and air bubbles. The first mechanism considered bubbles being precipitated on particle surfaces from gas-supersaturated zones in a flotation machine. The other considered collision of the particle with the bubble before their attachment. The collision mechanism becomes more widely accepted after the publication of Sutherland's paper in 1948. The stream functions used to model the probability of collision by earlier researchers were only applicable to limited bubbles: either too large or too small. Later on, Derjaguin and Dukhin (1961) proposed the famous "Three-Zone" theory – the space around the bubble is divided into three zones, defining zone 1 as the entire liquid outside zone 2 and zone 3; zone 2 comprises the forces due to diffusio-phoretic effects; and zone 3 is the closest to the bubble, where ordinary electrostatic and van der Waals forces are involved. Comparatively, the recently developed models are more useful for bubbles with sizes often used in flotation (Yoon and Luttrell, 1989). A critical review of the various models for the calculation of the collision efficiency between particles and bubbles was carried out by Dai et al. (2000). It was found that good agreement between the calculated and experimental collision efficiencies was obtained only with the Generalized Sutherland Equation. Using the bubble-particle collision mechanism, the slow kinetics of fine particles flotation can be well explained by the reduction in the frequency of bubble-particle collisions, P_c , with decreasing particle size.

In comparison, the process of adhesion is relatively less understood. The adhesion is essentially controlled by the chemistry of the system, which makes it

difficult to model mathematically. It is now considered that P_a is a function of the chemistry of the system (Yoon, 2000), the size of particles and bubbles (Yoon and Luttrell, 1989), all determining the rupture of the disjoining film between the air bubble and the particle. It is therefore related to the induction time (Laskowski, 1974; Luttrell and Yoon, 1988; Yoon and Luttrell, 1989). Despite the difficulties involved in studying P_a , induction time measurement through experiments under different chemical environments makes it possible to determine the probability of the particle-bubble adhesion. It has been clearly stated that the probability of bubble-particle adhesion, P_a , is connected to the induction time. Luttrell and Yoon (1988) utilized induction time measurements to determine the probability of bubble-particle adhesion and provided an expression for the probability of adhesion, i.e.

$$P_a = \sin^2 \left[2 \arctan \exp \left\{ \frac{-(45 + 8 \text{Re}^{0.72}) U_b t_i}{30 R_b (R_b / R_p + 1)} \right\} \right] \quad (\text{Equation 2-8})$$

where Re is the Reynolds number of the particle; U_b is the bubble rise velocity; R_b and R_p are the radius of the bubble and particle; and t_i is the induction time. Equation 2-8 suggests that P_a increases with decreasing particle size, and also with decreasing induction time. In this way, the efficiency of bubble-particle adhesion, P_a , is correlated quantitatively with the physical parameters such as the bubble size and particle size. It is worth to note that hydrodynamic factors had also been taken into account in Equation 2-8 by including Re , U_b and t_i . The P_a values predicted from the measured induction time are in good agreement with the flotation results obtained from the microflotation tests. The classical DLVO theory considers only the

electrostatic and dispersion forces. Recently, it was proposed that a third force, hydrophobic force, was responsible for the rupture of the wetting film during flotation (Xu and Yoon, 1989; Yoon and Mao, 1996; Yoon, 2000). Atomic force microscope (AFM) has been used to measure surface forces between hydrophobic surfaces (Liu et al., 2003). Understanding of hydrophobic forces of both particles and bubbles allows prediction of the adhesion probability using various surface chemistry parameters.

P_s , which is also referred to as $1 - P_d$, is taken as a function of contact angle, the size of bubbles, and the size and density of particles (Morris, 1950; Laskowski, 1974). Essentially, P_s can be correlated to the forces of adhesion between bubble and particle. Unfortunately, not too much information on P_s is available in open literature.

In terms of bitumen flotation, the probability of bitumen aeration is the product of the probabilities of collision (P_c), attachment (P_a), and retention (P_r) (Kasperski, 2001). P_c is determined by the hydrodynamic conditions, P_a by interfacial forces, and P_r is a function of the contact angle and turbulence in the liquid. It was proposed by Schutte (Kasperski, 2001) that factors that favor flotation are: (1) short induction time, (2) bitumen free of solid particles, (3) optimal size of bituminous droplets, and (4) high collision frequency, which is a function of the viscosity of the medium and relative viscosities of particles and bubbles.

In general, induction time is not only a function of the chemistry of the system,

but also a function of the hydrodynamics and physical parameters used in induction time measurement. Based on induction time measurement, the probability of adhesion can be predicted based on the stream functions. Using probability functions, a power relationship between flotation rate constant and bubble size was derived (Yoon, 2000). For example, contact time and induction time were used to study the floatability of coals of different ranks in Hallimond-tube flotation (Ye and Miller, 1988). The predicted floatability by the suggested model, which includes the calculated contact time together with the measured induction time, was found in good agreement with the experimental flotation recovery. Through the flotation experiments of fine coals treated with various levels of dispersed collector, a close correspondence between the flotation recovery and the induction time was obtained. Measured induction time also correlated closely with the mean critical wetting surface tensions for these dispersed collector-treated coals (Peng, 1996). Induction time has already been used to characterize the flotation behavior and good agreements have been showed between the measured induction time and the flotation recovery.

2.5 Recovering bitumen from oil sands

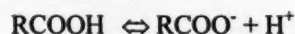
Athabasca oil sands deposit represents the largest bitumen resource in the world. The total oil in the oil sands deposit in Alberta province is even larger than total proven oil reserve in Saudi Arabia. Oil sand ores exhibit a wide variability and thus, different processability. The bulk composition of a given oil sand ore and some

of its properties are largely determined by its geological origin (Shaw et al., 1994). The composition and structure of oil sands are the decisive factors that affect bitumen recovery by flotation.

The Clark Hot Water Extraction process has been employed in the commercial operations to recover bitumen from the associated sand grains. The water-wet nature of the sand grains is the essential condition that makes the hot water-based processes work. According to what was proposed by Takamura (1985), connate water in oil sands matrix exists as pendular rings at the grain contact points and also as a roughly 10nm thick film covering sand surfaces. The disjoining pressure of the aqueous film is composed of three parts: electrical double layer repulsive force, London-Van Der Waals force, and short range interaction forces, such as hydration forces. Different steps are involved in bitumen recovery, which, in sequence, include oil sand lump size reduction, bitumen liberation from sand grains, formation of water-bitumen-air three phase contact line, bitumen recession and disengagement from sand grain surface, bitumen aeration, and finally flotation of aerated bitumen to form bituminous froth.

It is considered that several factors, such as the mechanical energy input, viscosity of bitumen, surfactant release and electrolyte concentration, etc., will affect the process of bitumen liberation from the sand grains (Masliyah et al., 2004; Zhou et al., 2000; Dai and Chung, 1995; Schramm et al., 2003; Drelich et al., 1993; Hupka and Miller, 1991). Three physicochemical properties of bitumen: viscosity, surface

tension, and interfacial tension, are expected to be of great importance in bitumen liberation (Drelich and Miller, 1993; Schramm and Smith, 1985, 1987; Schramm et al., 2003; Smith and Schramm, 2003; Isaacs and Morrison, 1985; Puig et al., 1979). The interfacial properties are greatly influenced by the surfactants released during conditioning period and the electrolytes present in slurry. Bitumen surfaces are negatively charged. According to the surface ionization theory (Takamura and Chow, 1985), the surface charge of the bitumen-water interface is generated from the dissociation of carboxyl groups that are naturally present in the bitumen:



The dissociation constant, K_a , is given by

$$K_a = \frac{[\text{RCOO}^-][\text{H}^+]_s}{[\text{RCOOH}]} \quad (\text{Equation 2-9})$$

where $[\text{H}^+]_s$ is the hydrogen ion concentration in the vicinity of the charged group and can be related to the bulk hydrogen concentration, $[\text{H}^+]_b$, by

$$[\text{H}^+]_s = [\text{H}^+]_b \exp(-y_0) \quad (\text{Equation 2-10})$$

and

$$y_0 = \frac{e\psi_0}{kT} \quad (\text{Equation 2-11})$$

where e is the electron charge, ψ_0 is the surface potential, k is the Boltzmann constant and T is the absolute temperature. This equation implies that hydrogen ions are preferentially accumulated near the bitumen surface because of the columbic attraction between positive hydrogen ions and the negatively charged surface.

The electrokinetic behavior of bitumen is believed to play a significant role in bitumen liberation from sand grains. As indicated by surface ionization theory, the electrokinetic behavior of bitumen is mainly governed by the interaction of the polar groups on bitumen surface with aqueous media. Knowing the electrokinetic behavior of bitumen will help to understand the effect of different pH and calcium concentration on bitumen liberation. Through atomic direct force measurement between bitumen and silica, it was confirmed that liberation of bitumen from sand grains is difficult in a low pH environment due to the strong adhesion force (Liu et al., 2003). It was found that optimal recovery efficiency was associated with a maximum interfacial electric charge and a minimum interfacial tension (Schramm et al., 2003). Lowering the bitumen-water interfacial tension through increasing pH by addition of small amount of caustic or $\text{Na}_5\text{P}_3\text{O}_{10}$ could increase the amount of bitumen recovered (Drelich and Miller, 1993).

Research found that other factors could also affect the bitumen liberation significantly under some circumstances. Lab experiments showed that pretreatment of oil sand ore with kerosene (10 wt% kerosene) or the use of MIBC/kerosene was beneficial to bitumen liberation, thus, bitumen recovery (Basu et al., 1997, 1998; Drelich and Miller, 1993). More recently, it was also found that both the indigenous air bubbles that act as activators to the attachment of larger air bubbles and an air addition during oil sand conditioning period would be beneficial for bitumen liberation from sand grains (Flynn et al. 2001). Significant bitumen recovery from

Whiterocks oil sand was observed only when the slurry was sparged with air during digestion (Drelich et al, 1995). These results suggest that, in the future design, it will be beneficial to entrain an adequate number of properly sized air bubbles through air sparging during digestion period so that the overall bitumen recovery could be improved. This concept has not been fully realized in the traditional slurry equipment design. Recently, the role of gas nuclei present in the oil sands slurry catches more attentions. Even though the amount of gas nuclei in the slurry may not be sufficient to effectively recover bitumen from oil sand ores, their role in bitumen liberation from the sand grains and enhancing bitumen-air attachment should not be ignored (Masliyah et al., 2004). Gu et al. (2004) demonstrated the role of gas nuclei during their study in the attachment of hydrogen bubbles to a stationary bitumen droplet. It is assumed that the presence of tiny air bubbles would help to break the thin water films.

Following bitumen-solid separation, bitumen-air attachment is essential. However, there is no reason to believe that bitumen liberation and bitumen -bubble attachment occur sequentially. Instead, it is very likely that air-bitumen attachment can take place as long as bitumen and air are available to each other (Masliyah and Gray, 2003). It is necessary for the liberated bitumen droplets to attach to air bubbles in order to float them because the density of bitumen within the operating temperature range is almost the same as that of water. It is considered that bitumen either attaches to or spreads over the air bubble surface after it makes attachment to the air bubble and this has been proved through the on-line visualization of flotation systems or

through microscopic observations (Malysa et al., 1999; Drelich et al., 1995). When bitumen-bubble attachment is established, it is expected that bitumen can spread onto the air bubble to favor bitumen liberation and aeration. Based on the thermodynamic criteria, the spreading of a fluid onto a substrate can be predicted by the so-called spreading coefficient S : a positive S implies spontaneous spreading of the liquid, while a negative one suggests 'beading' on the surface (Adamson and Gast, 1997, Moran et al., 2000). For the case of bitumen-air-water system, the appropriate expression of the spreading coefficient S should be:

$$S = \gamma_w - (\gamma_b + \gamma_{bw}) \quad \text{(Equation 2-12)}$$

where γ_w and γ_b are respectively the surface tension of water and bitumen, and γ_{bw} is the interfacial tension between bitumen and water. This equation measures the tendency for bitumen to spread onto air-water interface. A positive spreading coefficient implies that the aeration of bitumen will proceed as a spontaneous process, as long as the bitumen-air contact is established, until the air bubble is completely engulfed by bitumen. Spreading coefficient S calculated from equilibrium values of the surface tension of water and bitumen and the interfacial tension of bitumen-water remains positive for a varying pH range and inorganic salt concentration (Drelich et al., 1995). Based on this statement, it appears that bitumen and bubble attachment should happen spontaneously. However, the attachment of bitumen to air bubble is affected by the wettability of bitumen and air bubble, which is affected by slurry chemistry and fine solids and/or clays attached to bitumen and/or air surfaces. Fine solids-bitumen and fine solids-air attachment is controlled by electrostatic repulsive

forces between fine solids-air and fine solids-bitumen, which in turn is affected by the type and surface potentials of the fine solids, air and bitumen, as well as the concentration of electrolytes and pH of the slurry (Masliyah and Gray, 2003; Dai and Chung, 1995). The coating of hydrophilic clays on a naturally hydrophobic bitumen droplet inevitably depresses bitumen flotation by setting up a barrier for bitumen-bubble attachment. This adverse effect is triggered by the increase of the calcium concentration in the flotation system. It has been reported that the presence of a small amount of multivalent cations spoils the efficiency of the hot water separation process (Takamura, 1985). Recent studies have shown that, even though neither the increase of calcium alone up to 40 ppm nor the addition of 1 wt% montmorillonite imposes any significant impact on bitumen recovery. However, the addition of 1wt% montmorillonite clays with calcium ion concentration above 30ppm causes a sharp reduction in bitumen recovery (Kasongo et al., 2000). This reduction in bitumen recovery is attributed to the adsorption of calcium ions on montmorillonite clays. These calcium ions interact with the carboxylic groups of natural surfactants on bitumen droplets or released into solution to form insoluble calcium carboxylate, causing the clays to coat on the bitumen. The coated clays remain hydrophilic, thereby reducing bitumen-bitumen coalescence and air-bitumen attachment with clays as steric barrier. Through zeta potential distribution measurement, it is clearly shown that the addition of calcium ions greatly reduced zeta potential of bitumen (less negative) to zero, depending on the concentration of calcium (Liu et al., 2003). It is clear that water chemistry is an important factor affecting bitumen-bubble attachment.

For this reason, recycled water or tailing water management is a subject deserving further study.

Surfactants, their release and interfacial tension have been of great interest to researchers because of their importance in bitumen liberation and aeration. The surfactants released from oil sands, with the addition of NaOH, are predominantly water-soluble salts of naphthenic acids having carboxylates functional groups (Schramm and Smith, 1985, 1987). The Surface Ionization Model was proposed to explain the electric properties of the bitumen-water interface (Takamura and Chow, 1985). It is believed that clays and polyvalent compounds in the form of carbonate and sulfates contained in the oil sands react with the added NaOH. Therefore, the release of natural surfactants would be interfered by multivalent cations since the polyvalent compounds consume hydroxide to compete with the surfactant-forming reactions and precipitate carboxylate surfactants (Smith and Schramm, 1992). The effect of natural surfactant released from estuarine and marine oil sands on air holdup was investigated using a water column by Zhou et al. (2000). It was considered that the higher air holdup and poor processability of marine ores could be attributed to the release of large amount of surface-active species and the presence of more fine clays in the ores. This controversy effect of surfactant suggests that the role of surfactants released from the oil sands needs to be further studied in order to have a better understanding of how surfactants affect the liberation and/or aeration process.

An important goal of the flotation process is to produce bituminous froth, which is of multiphase, composed of oil, gas, water, and solids, without entraining large amount of solids and water, since the emulsified water and entrained solids in the froth cause adverse effect during the subsequent upgrading operations. Thus, producing high quality froth is of great interest. Experiments have shown that addition of a small amount of chemicals and demulsifiers (mostly water-in-oil emulsion breaking agents) can encourage coalescence and separation of water droplets from the bituminous froth (Schramm et al., 1998; Stasiuk and Schramm, 2001). Also, a combination of high HLB surfactants and solvents can significantly reduce the froth water content without sacrificing bitumen recovery (Shaw et al., 1994). However, since oil sands extraction is a closed loop: process water is recycled and used repeatedly, the cumulative effect of added chemicals on different extraction steps remains a big concern to industry operations.

Through about eighty years of research and commercial operations of oil sands extraction, the knowledge regarding the effect of operating parameters and bitumen properties on bitumen recovery has been accumulated with time. More recent studies have been focused on the interactions among various oil sand components and air bubbles by the adoption of advanced analytical instruments. Yeung et al. (1999) developed micropipette technique to measure interfacial properties of bitumen. It was used to investigate the bitumen-bitumen coalescence and bitumen-air bubble attachment at a micro-scale. Atomic force microscope was introduced into oil sands

study by Liu et al. (2003, 2004) to directly measure the intermolecular and adhesion forces between bitumen and fine clay particles or silica. Liu et al. (2003) investigated the factors affecting hetero-coagulation of bitumen and fine particles through an indirect method, zeta potential distribution measurement of colloidal mixtures. Induction time measurement was used to study the attachment of bitumen and various gas bubbles (Gu et al., 2003, 2004; Wang et al. 2003). A laboratory Hydrotransport Extraction System (LHES), invented by Oil Sands Extraction Group at the University of Alberta, is now accepted by researchers and industries to evaluate the performance of water-based oil sands extractions and role of different chemical aids. The LHES is believed to be able to mimic the commercial pipeline hydrotransport and low-temperature extraction processes well (Wallwork et al., 2003).

Despite the accumulated knowledge of oil sands and its extraction operations, the fundamental mechanisms of oil sands extraction processes are still not fully understood. One of the challenges facing industries is how to improve bitumen recovery from poor processing ores containing high content of fine clay particles and divalent metal ions. One of the areas that need to be further investigated is air-bitumen attachment. It was identified through experiments that air-bitumen attachment and flotation subprocesses are the rate limiting process in recovering of bitumen from oil sands. Another area getting more attentions is the measurement of interactive forces in multiphase systems of bitumen, water, solids, air, and chemical additives. These forces collectively determine not only the kinetics of conditioning and separation, but

also the deposition and densification of tailings. Understanding phenomena at the microscale level is necessary before mechanistic models of unit operation and processes can be developed. It is the trend and industrial requirement to develop less energy-intensive, more economical and environmentally sustainable extraction processes.

Since the Clark Hot Water Extraction process has been so successfully employed in a number of commercial operations, many of the advances in the technology and processes were a result of continuous improvement and therefore were incremental in nature. However, there were some important "step-changes" which involved important innovations. These were put into practice in the 1990's, which, in terms of mining and extraction operations, mainly includes the changeover from dragline/bucketwheel/conveyer mining to the more energy efficient shovel/truck/hydrotransport mining. Also, there is a shift toward a lower operation temperature and a caustic free process that has already been used in the design of Steepbank Mine and Millenium project at Suncor, and the North Mine and Aurora Mine at Syncrude.

Research driven by industry needs is ongoing into a wide variety of problem areas. Recently, a lot of efforts have been devoted to understanding the problem related to the poor bitumen flotation performance of poor processing ores and to finding new processes or process aids to improve bitumen recovery from poor

processing ores. Using oily bubbles flotation technology could be one of the solutions. The possibility and feasibility of adding hydrocarbon to an air stream in order to enhance bitumen-air attachment of poor processing ores and hence improve bitumen recovery were studied (Wallwork et al., 2003). The concept of using oily bubbles (bubbles coated with a thin layer of oil or solvent) in oil sands extraction came from the demonstrated success of oil-assisted processes in mineral flotation, especially coal flotation. It was demonstrated that bitumen recovery increased from ca. 10% to 98% for Suncor's oxidized ores and from ca. 20% to 65% for Syncrude's poor processing ores by using kerosene-coated air bubbles instead of air bubbles (Wallwork et al., 2003). The application of oily bubble flotation in oil sands industry is appealing. However, the mechanisms of how oily bubbles help enhance bitumen recovery from oil sands remains to be investigated, which is the objective of this research. To accomplish this objective, contact angle (Chapter 3) and induction time (Chapter 4) measurements were applied to bitumen flotation system by using oily bubbles.

3.0 CONTACT ANGLE MEASUREMENT

Flotation process utilizes the differences in physico-chemical surface properties of various mineral particles. Wetting phenomena are controlled by both the solid surface properties and wetting fluids. Early studies of wetting phenomena showed that the wetting properties of a solid were dominated by the outermost layer of molecules (Morrow, 1990). Contact angle is considered to be the most universal measure of the wettability of surfaces. For this reason, contact angle measurements have been the most widely used to evaluate the wettability of solid surfaces.

Contact angle was also used to assess the surface hydrophobicity of bitumen in a bitumen flotation system. The measured contact angle in bitumen-air-water system would serve as a marker to indicate how water chemistry affects the hydrophobicity and hence the floatability of bitumen. It was demonstrated that bitumen recovery by flotation correlates well with the measured contact angles for different oil sands ores: a larger contact angle corresponds to a higher bitumen recovery (Zhou, 2002). Contact angle measurement was also used to study the interactions between ionic species, precipitates, and fine solids with a low energy hydrophobic surface by using a model system of paraffin wax in aqueous solutions (Zhou et al., 1998). The results of contact angle measurements have been used to explain the detrimental synergistic effects of smectite clays and calcium ions on recovering bitumen from Athabasca oil sands by flotation (Kasongo et al., 2000). In a separate study, Liu et al. (2002) used contact

angle measurement to examine the selective attachment of reactive oily bubbles on targeted mineral particles. The results showed that the measured contact angle values of reactive oily bubbles on the responsive surfaces are generally much higher than those of conventional air bubbles, which translates to a stronger collecting power of reactive oily bubbles.

One challenge facing oil sands industry is the low bitumen recovery while processing poor processing ores. One of the potential solutions is to use oily bubbles instead of air bubbles for bitumen flotation. Earlier experimental results showed that, compared with conventional air bubbles, the bitumen recovery using kerosene-coated bubbles is greatly enhanced. It was speculated that the surface properties of air bubbles were changed drastically after being coated by a thin layer of liquid hydrocarbon. Since contact angle measurement has been the most commonly used method to examine the wettability of the surfaces and potency of attaching the surface to air bubbles, contact angles of oily bubble on bitumen in process water are measured to provide a guideline whether oily bubbles would help improve bitumen recovery through changing the contact angle between bitumen and bubbles in a slurry system.

3.1 Experimental

3.1.1 Preparation of bitumen surfaces and process water

To measure contact angle of bitumen attachment to an air or oily bubble in water, a thin layer of solvent-extracted bitumen (provided by Syncrude Canada Ltd.) was first spin-coated on a 2 x 2cm PTFE substrate by a spin coater (MODEL P6700, Maker) operating at 3,000rpm for 3 minutes. Bitumen coated as such had a mirror-like finishing, suitable for contact angle measurement. To avoid any contamination, a new substrate was prepared for each experiment of different solution conditions or using different type of bubbles.

To prepare process water, a 500g oil sand sample was mixed with 800ml deionized water (DI water) in a 1L Denver flotation cell. The slurry at 35°C was agitated at 1800rpm for 10 minutes, during which the froth was collected. A portion of the remaining suspensions was collected and subjected to centrifugation at 40°C and 20,000rpm for 1 hour to remove the suspended solids. The resultant clear supernatant was collected and used as process water in pertinent experiments. Three different types of ores, namely good processing ore, transition ore and poor processing ore, all provided by Syncrude Canada Ltd, were used to obtain corresponding process water with the procedures described above. For comparison, the recycle Aurora water, also provided by Syncrude Canada Ltd, was used in a number of tests. Detailed information of ore composition and water chemistry for different types of water is

given in Table 3-1 and Table 3-2.

Table 3-1 Water chemistry of process water from different types of ores

Water chemistry	Process Water			
	Good ore	Transition ore	Poor ore	Aurora recycle water
Ca ²⁺ (ppm)	0.7	6.5	20.1	42.6
Mg ²⁺ (ppm)	0.6	5.8	11.5	16.5
pH	7.4	7.8	8.1	8.9
Surface Tension (mN/m)	66.5	67.1	68.3	65.2

Table 3-2 Composition of oil sand ores (in wt %)

Composition	Good ore	Transition ore	Poor ore
Bitumen	14.5	9.3	5.9
Solid	84.4	83.5	87.0
Water	1.1	7.2	7.1

3.1.2 Experimental techniques

The bitumen coated PTFE substrate was placed into a square glass cell containing deionized water (pH 6.5) or process water obtained from processing of different types of ores. The temperature of water was controlled by a water bath jacket surrounding the glass cell. The captive bubble method was used to measure contact angles through water phase using a video-assisted NRL Rame-Hart goniometer (see

Figure 3-1). In this case, an air bubble was generated at the tip of a micro-syringe (25 μL , without needle) and kept in the solution for a given period of time before being brought into contact with the bitumen surface. To minimize the changes of contact angles with different bubble sizes as reported by Drelich et al. (1993), a bubble of relatively large volume (2-5 μL) was used in this study. The bubble was allowed to remain between the syringe tip and bitumen surface for a sufficient period of time, until equilibrium was reached, judged by an invariant contact angle with contact time. To avoid the bubble moving around during changing the bubble volume via pulling or pushing the plunger (see Figure 3-1), the formed bubble was constrained between the bottom surface of the syringe and the substrate. The entire process was recorded on videotapes and replayed later on for contact angle measurements. The dynamic contact angle and the contact angle after an extended period of contact between the bubble and bitumen were measured at three phase contact points on both (left and right) sides of recorded images. Initial contact angle value was measured as soon as the three phase contact line was established, or the attachment of air bubble to bitumen surface was observed, judged by a sudden expansion of contact area between the bitumen and air bubble. At least four independent measurements at distinct locations were made with the average being reported in this thesis. Since the contact angles were measured during expansion of bitumen-bubble contact area after attaching an air bubble to a bitumen surface in water, water was displaced from bitumen surface during contact area expansion. The contact angle determined as such is referred to as receding contact angle in this thesis. Such a process is more akin to

the bubble-bitumen attachment process encountered in flotation and more relevant to industrial bitumen flotation. For this reason, only receding contact angle values are reported in this thesis, unless otherwise indicated.

To examine the effect of bubble aging time on contact angle measurement, a set of baseline experiments was conducted. Virtually no change was observed for the aging time from 10 to 30 min. Therefore, a 15-min equilibrium period was used in all the contact angle measurements.

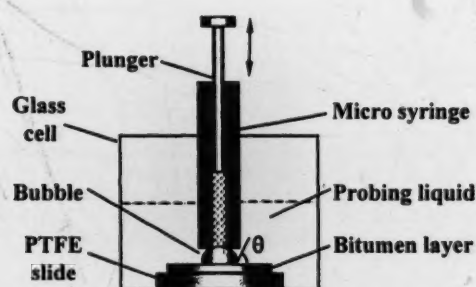


Figure 3-1 Schematic of experimental setup for contact angle measurement

To measure the contact angle of oily bubbles on bitumen surface, a thin layer of oil or solvent, either kerosene, toluene, heptane or naphtha, purchased from Fisher, was spread on the top of test aqueous solutions. For easy discussion, we refer air bubbles covered with a thin layer of oil or solvent collectively to oily bubbles. To generate an oily bubble, an air bubble of a desired size was generated in the oil or

solvent phase using the micro-syringe. The bubble was then brought across the oil (solvent)-water interface to form an oily bubble in the aqueous phase. The oily bubble was allowed to equilibrate in aqueous solution for a given period of time as in the case of air bubbles, followed by the same procedures used to measure the contact angle of air bubbles, except that, in this case, the air bubbles were covered with a thin layer of hydrocarbons.

In this study, contact angles of air bubbles and oily bubbles (coated with kerosene, naphtha and toluene) in deionized water were measured at 35°C and 50°C to allow the interpretation of the results from bitumen extraction tests. Contact angles of air bubbles were also measured at room temperature in deionized water and process water from different types of oil sand ores.

3.2 Results and Discussion

3.2.1 Contact angles measured in deionized water

As a baseline, contact angles between bitumen and air bubbles were measured in deionized water. To determine whether and how the thin layer of oil or solvent coated on air bubbles change the surface properties of air bubbles, contact angle of different oily bubbles on bitumen in deionized water was also measured. Three kinds of liquid hydrocarbons (toluene, kerosene and naphtha) were used to generate oily bubbles. The initial and pseudo equilibrium receding contact angles measured at 35°C

and 50°C are summarized in Figures 3-2 and 3-3, respectively.

3.2.1.1 Air bubbles

When water temperature was increased from 35°C to 50°C, the initial contact angle increased sharply from 26.7° to 35° as shown in Figure 3-2. A comparison of Figure 3-2 with Figure 3-3 shows a much larger receding contact angle than corresponding initial contact angle for both temperatures. However, the receding contact angle increased only slightly with temperature from 86.1° to 88.6° as shown in Figure 3-3. Considering the measurement errors, this level of variation in receding contact angle with temperature in the range examined could be considered negligible.

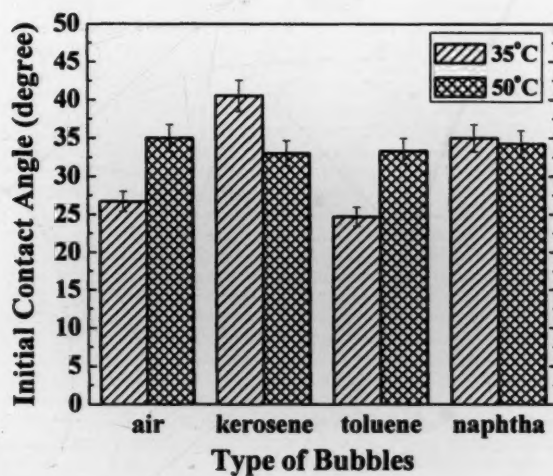


Figure 3-2 Initial contact angles of air/oily bubbles on bitumen in deionized water

The larger initial contact angles at higher temperature suggest that high temperature is beneficial for the establishment of the three phase contact line between bitumen and bubbles in water. On the other hand, temperature does not bear any significance in the receding contact angle. Since the reported receding contact angle values are obtained after a prolonged contact between air/oily bubbles and bitumen, these values are believed to be dependent on the interfacial tension only as shown in the well-known Young's equation. The observed invariance of receding contact angle with temperature is in accordance with the documented fact that the bitumen-water interfacial tension does not change substantially within the temperature range examined.

3.2.1.2 Oily bubbles

Figure 3-3 shows that when the temperature increased from 35°C to 50°C, the receding contact angles changed only slightly for all three kinds of oily bubbles, similar to the case of air bubbles. However, the initial contact angle varied substantially for toluene and kerosene coated oily bubbles but not for naphtha-coated oily bubbles. It is important to note a decrease in the initial contact angle of kerosene coated oily bubble on bitumen from 40.5° to 33° with increasing temperature from 35°C to 50°C. This decrease may be attributed to an increased solubility of bitumen in kerosene with increasing temperature. At 35°C, kerosene-coated oily bubble exhibits the largest initial contact angle, followed by naphtha- and toluene-coated oily bubbles.

When the receding contact angle values of air bubbles on bitumen are compared with that of oily bubbles, the difference can be considered to be negligible for both temperatures. However, the initial contact angle value for kerosene is significantly higher than that of air bubbles at lower temperature of 35°C. This finding suggests that use of kerosene oily bubbles at low process temperature may well be beneficial for establishing the three phase contact between bubble-bitumen in water, although the final state of attachment may be the same in both cases.

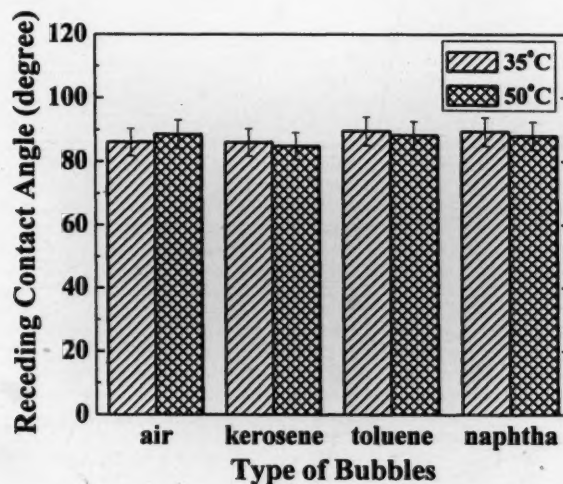


Figure 3-3 Receding contact angles of air/oily bubbles on bitumen in deionized water

3.2.1.3 Spreading dynamics

The results above show that at a given temperature, there is no significant difference in the receding contact angles between air bubbles and oily bubbles. In bitumen flotation, a system with a larger contact angle has been reported to

correspond to a higher bitumen recovery. Clearly, the above mentioned results cannot provide a justification for the use of oily bubbles to improve bitumen recovery rate from poor processing ores, which had been demonstrated by laboratory tests (Wallwork et al., 2003). In order to reconcile this apparent conflict, the attention was directed to spreading of bubbles on bitumen surfaces in deionized water. It was observed during the contact angle measurement that oily bubbles spread faster on bitumen surface than air bubbles after establishing bitumen-bubble contact. In order to quantify the effect of oil or solvent film around air bubbles on the spreading speed of the bubbles on bitumen surface, the changes of contact angles with time after the establishment of three-phase contact line, i.e. dynamic contact angles, were measured for both air bubbles and oily bubbles. The results are shown in Figure 3-4.

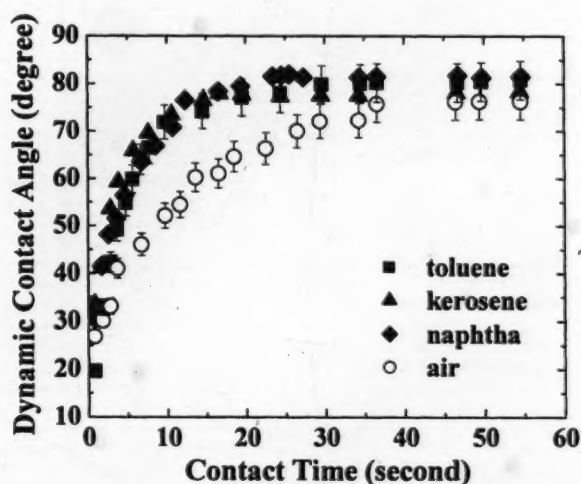


Figure 3-4 Dynamic contact angles of air/oily bubbles on bitumen in deionized water

From the results shown in Figure 3-4, it is evident that the increase in receding

contact angles for all three types of oily bubbles is much faster than that for the air bubbles, although eventually they all reach a similar contact angle value of 80° . For oily bubbles, the receding contact angles reached the maximum after about 15 seconds of the initial attachment of bubble on bitumen, in contrast to 40 seconds for air bubbles. The improvement in spreading of oily bubble in comparison to air bubble over a bitumen surface may be attributed to a greatly reduced viscosity of bitumen at the contact region by toluene, kerosene and naphtha coated on air bubbles, leading to a decreased resistance to the expansion of three phase contact lines and hence an improved attachment kinetics of oily bubbles to bitumen surfaces. Therefore, although the ultimate contact angles for the air bubble and oily bubbles are almost the same, the increased spreading dynamics of oily bubbles on bitumen surface will be beneficial to bitumen recovery from oil sands, in which bubble-bitumen contact time is rather limited, depending on the hydrodynamics of the system. Fast spreading ensures the oily bubble-bitumen attachment to reach a stable state of a larger contact angle within the time frame available for bubble-bitumen contacts in a dynamic flotation system. Considering a relatively short period of each bubble-bitumen contact in a flotation cell, using solvent-coated air bubbles would be beneficial for improving the rate of bitumen-bubble attachment. Consequently, the recovery of bitumen from oil sands will be enhanced.

3.2.2 Effect of Water Chemistry

Contact angles for air bubbles on bitumen in different types of process water were measured at room temperature with the intent to determine the effect of water chemistry on air bubble/bitumen attachment and bitumen flotation. Four different types of process water as listed in Table 3-1 were used. They were Aurora recycle water, and process water (PW) from good processing ore, transition ore and poor processing ore. Figure 3-5 shows that the receding contact angle in deionized water is the largest (about 90°), followed by that in three process water from good processing, transition and poor processing ores (about 80°). The receding contact angle in the Aurora recycle water is the smallest (about 75°).

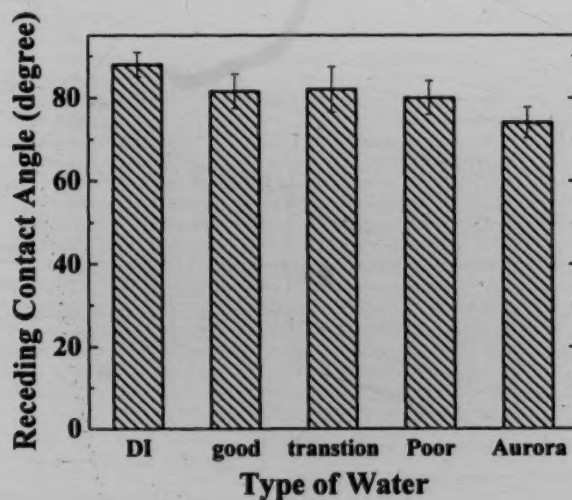


Figure 3-5 Effect of water chemistry on receding contact angle of air bubbles on bitumen in process water

The reason why contact angle measured in the Aurora recycle water is the smallest may be attributed to a higher concentration of accumulated surfactants in the recycled water as compared with that in the freshly prepared process water from all three types of oil sand ores. A high concentration of surfactant brings down bitumen-water interfacial tension as well as surface tension of recycled water. As a result, air bubble-bitumen attachment may be reduced as reflected by a smaller contact angle of air bubble on bitumen. However, the measured contact angles of air bubbles in process water prepared using three different types of oil sand ores were almost the same, although bitumen recovery for different types of ores are known to be greatly different. This might be caused by the removal of suspended solids from the process water when preparing water samples for contact angle measurement. Bitumen recovery for good processing ores can be as high as 95%, and that for poor processing ores may be as low as 20%. It is clear that such difference in bitumen recovery may not be predicted by the results of contact angle measurements. We can conclude in this case that contact angle is not sufficiently sensitive to reflect changes of bitumen recovery with changing water chemistry, although it can serve as a good measurement of the surface properties for most cases. To better understand the role of oil or solvent film around air bubbles in enhancing bitumen recovery from poor processing ores, induction time of dynamic nature was measured as reported in the next chapter.

3.3 Conclusions

Temperature has a marginal effect on receding contact angles for both air bubble and oily bubbles. However, the initial contact angles increase with increasing temperature except for kerosene-coated bubbles, which may be attributed to an increased solubility of bitumen in kerosene with increasing temperature. Increasing temperature will also improve the spreading of air bubbles on bitumen surface. At 35°C, kerosene-coated oily bubble exhibits the largest initial contact angle among the three different kinds of oily bubbles, which may be beneficial for establishing the initial three phase contact between bitumen-bubble in water.

Receding contact angle values are almost the same for oily bubbles and air bubbles. However, oily bubbles spread faster than air bubbles on bitumen surface after establishing bitumen-bubble contact. The increased spreading dynamics may be due to the greatly reduced bitumen viscosity by oil or solvent at the contact region, resulting in a decreased resistance to the expansion of three phase contact lines, which would help enhance bitumen recovery by flotation.

Contact angle sometimes may not be sensitive to the changes of the flotation system as indicated by the experimental results. Thus, other methods, such as induction time measurement, should be used in such circumstances to further investigate the mechanisms of how oily bubbles help improve bitumen recovery.

4.0 INDUCTION TIME MEASUREMENT

Among all the subprocesses in flotation, the attachment of mineral particles to air bubbles is the most fundamental requirement for successful flotation. This process involves the thinning and rupture of the wetting film between the colliding particles and air bubbles. The minimum time required for the film to drain to a critical thickness and rupture spontaneously to form a stable bubble-particle aggregate is defined as the induction time (Yoon and Yordan, 1991). Extensive research has been devoted to determining the factors affecting the measurements of induction time; setting up models to describe the processes of water film thinning, film rupture, and TPC expansion; understanding the particle-bubble attachment in flotation; and finally correlating the measured induction time with the flotation recovery (Gu et al., 2003; Wang et al., 2003; Yoon, 2000; Laskowski, 1974; Eigeles and Volova, 1960; Yoon and Yordan, 1991; Pugh and Yoon, 1994; Peng, 1996; Ye and Miller, 1988; Fan et al., 1989). Since induction time reflects kinetics and is linked with hydrodynamics of a flotation system, it is measured in this study to explore the mechanism how oily bubbles help improve bitumen recovery from poor processing ores. It is well documented that the measured induction time depends not only on the chemistry but also on the physical and hydrodynamic characteristics of a measurement system (Gu et al., 2003). This is taken into account in this study by fixing physical parameters in attempt to emphasize the effect of water chemistry on bubble-bitumen attachment.

4.1 Equipment set-up and experimental method

4.1.1 Equipment set-up

The set-up for induction time measurement used in this study was an improved version of that used by Gu et al. (2003). A schematic of the setup is shown in Figure 4-1. In this set-up, a 5" 2-way speaker (40watt) with a frequency range of 90-15,000 Hz was used as the power drive. The movement of an air bubble was controlled by the drum of the speaker via a capillary tube of 0.89mm I.D. and 1.33mm O.D. One end of the capillary tube is attached to the drum of the speaker with the other end holding the air bubble. The air bubble of a controllable size was generated at the end of the capillary tube by a Gilmont micro-syringe (GS-1200, 2.0mL) to a 0.5% accuracy. Pulnix ½" format B&W CCD camera and a 40x lens were used to assist the precise positioning, control of bubble sizes, and to capture the approaching and retracting process of an air bubble toward and away from a bitumen surface. An amplifier interfaced with a computer was used as a power source to drive the speaker and hence the air bubble attached to the capillary tube. A micro-displacement sensor (Omron Z4DF04A) with 5V power supply was used to detect the actual displacement of the speaker's drum. A PC1-6036E data acquisition (DA/AD) board purchased from National Instruments was installed on a desktop computer. A customer-designed software allowed instructions to be sent to the controller and signals to be received from the sensor in real time. The software program was developed by Dr. Guoxing Gu in our group using National Instruments LabView 6i. The details on the program

control panel and the program diagram are given in appendix. A timer on the data acquisition board was programmed to generate 10,000Hz time pulse to ensure a precision of 0.1ms. A three-way X-Y-Z positioning stand with 70mm X travel, 60mm Y travel, and 65mm Z travel was used to position and align the samples held in the square glass cell in relation to the bubble above.

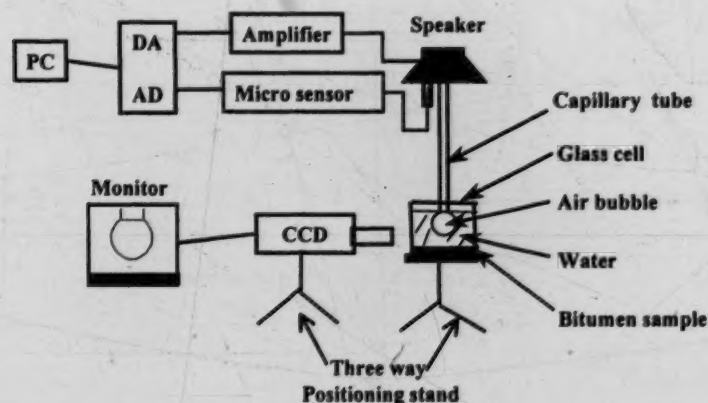


Figure 4-1 Schematic of equipment setup for induction time measurement

A basic requirement for using a speaker as a power driver is that the displacement of the speaker drum must have a linear correlation with input voltage. This was checked by measuring the real displacement of the speaker drum as a function of input voltage, which is actually translated into the movement of the capillary tube attached to it. Therefore, the displacement of the capillary tube with different input voltage was measured. Figure 4-2 shows that, over the whole range of input voltage (0V – 5V), the measured displacement is linearly dependent on the voltage input. The maximum voltage input, 5V, corresponds to the maximum capillary

displacement of 0.85mm.

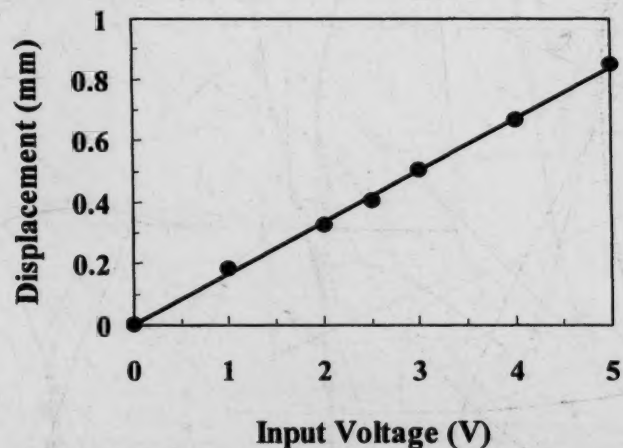


Figure 4-2 Dependence of capillary displacement upon input voltage

4.1.2 Experimental method

The coker feed bitumen sample (provided by Syncrude Canada Ltd.) was stored in a refrigerator at about -20°C . After taking the bitumen sample out of the refrigerator, it was left at room temperature for about 30 minutes. When the bitumen was softened, a fixed amount of bitumen was pasted onto the inner bottom of a square glass cell (35mmx35mmx55mm) using a spatulator. Then, the glass cell with bitumen was heated up to about $70-80^{\circ}\text{C}$ on a hot plate in order to form a smooth and mirror-like bitumen surface. After the glass cell was cooled down to room temperature, a fixed amount of deionized water or process water prepared using the same method as that used in contact angle measurement was added into it. It is known that surface tension and interfacial tension have a great effect on induction time. It was reported

that, in the presence of surfactants, the equilibrium interfacial tension (IFT) between two immiscible fluids could be very dependent on the particular technique used for measurement (Yeung et al., 1998). The partitioning of surfactants between the two bulk phases, such as bitumen and water, and the interface, which ultimately determines IFT, depends on geometric factors such as the volume fractions and specific interfacial areas (i.e., interfacial areas per unit volume) of the two fluids. For the purpose of this project, no further systematic study was carried out to investigate the effect of geometric factors on induction time for the current water-bitumen systems. Instead, to eliminate the effect of surfactant partitioning on equilibrium IFT, volume fractions and specific interfacial areas were fixed at 1g bitumen coated on the inner bottom of the glass cell holding 40ml water for all the induction time measurements.

During the experiments to measure induction time using an air bubble-silica particle model system, Gu et al. (2003) found that the measured induction time was highly dependent on the physical and mechanical parameters used in the measurement. The parameters examined in their studies included the initial gap (h_0) between the air bubble and the particle bed, the displacement (H_0) of the air bubble holder, the diameter (d_b) of the air bubble, and the velocities of the air bubble approach (U_a) to and retraction (U_r) from the particle bed. In addition, density and contact angle of the particles, density, viscosity and surface tension of the liquid and the three-phase contact line tension are all among the factors that affect the result of induction time measurement.

Since the objective of this study was to investigate the role of the oil or solvent film coated on air bubbles through induction time measurement, physical and mechanical parameters were fixed for all the experiments of induction time measurement in order to eliminate their effect on the experimental results. The initial gap between the air bubble and bitumen surface (D_g) was 0.15mm. The velocities of the air bubble approaching (U_a) to and retracting (U_r) from the bitumen surface were fixed at 5cm/s. The displacement (D_c) of the air bubble holder was 0.25mm. The bubble size (D_b) was kept at 1.5mm unless otherwise specified (shown in Figure 4-3). The error for the bubble generation was controlled within 1%, aided by the CCD camera macro lens. With this system, the image of the air/oily bubble displayed on the monitor was magnified by 40 times of the real bubble size.



Figure 4-3 Schematic of the measurement of induction time

The bitumen sample coated on the inside bottom of the glass cell was incubated in the water held inside the glass cell for two hours before carrying out induction time measurements. The justification for two hours' incubation time will be given in 4.2.1. The main purpose was to let the bitumen-water system reach pseudo-equilibrium state so that reliable and repeatable experimental data could be

obtained.

An air bubble of a controllable size was generated in the water at the end of the capillary tube by a Gilmont micro-syringe (GS-1200, 2.0mL). A preset contact time was input to the LabView 6i program control panel. The contact of the bubble towards bitumen surface was made by driving the capillary tube attached to the speaker drum. The preset contact time started at a small value while observing whether bitumen-bubble attachment was established. The preset contact time was progressively increased until bubble attachment to the bitumen surface was observed. The minimum time required to establish such an attachment is considered to be the induction time.

For the cases of oily bubble-bitumen attachment, oily bubbles were generated using the same method as described for contact angle measurement. All the other experimental procedures were the same as those used for induction time measurement of air bubble-bitumen attachment.

4.2 Results and discussion

4.2.1 Effect of bitumen aging on induction time measurement

The induction time of an air bubble attaching to a bitumen surface in deionized water was measured with the intention to use it as the baseline for comparison purpose. The induction time measured for a given system was found to decrease with increasing incubation time of bitumen in the deionized water, as shown by the results in Figure 4-4. It should be noted that time "0" in this figure indicates the moment when water was added into the glass cell with bitumen being coated on its inner bottom surface. This is the moment that bitumen is made in contact with water. Figure 4-4 shows a decrease in the induction time from 1800 ms to 1100 ms with incubation time from 20 minutes to 120 minutes, after which a negligible change in the measured induction time was observed with further increasing incubation time. This finding proved that induction time measurement reflected both the surface properties of bitumen and, more importantly, the interfacial properties of bitumen/aqueous interfaces.

The transfer of natural surfactants from bitumen to bitumen-water interface and into aqueous phase is considered to be the main reason for the observed decrease in the measured induction time with increasing incubation time. When bitumen is in contact with water, the natural surfactants released from the bitumen tend to accumulate at the bitumen/aqueous and air/water interfaces (Schramm et al., 1985,

1987, 1992; Issacs and Morrison, 1985; Yeung et al., 1999). The accumulation of the surfactants at the interfaces not only reduces both bitumen-water and air-water interfacial tensions, but also imparts surface charges at the interfaces, mainly arising from the dissociation of acid groups at the interface. This later effect has been demonstrated in earlier studies (Liu, et al., 2002) and explained by surface site ionization model (Takamura and Chow, 1985). Isaacs and Smolek (1983) performed a systematic study on the effect of process variables, such as temperature, salinity, alkalinity, surfactant type and aging, on the bitumen-water interfacial tension. One of their major findings was that the interfacial tension was sensitive to the age of surfactant preparation. For the systems investigated, the interfacial tension decreased rapidly with time, until a critical plateau value was reached. It is interesting to note

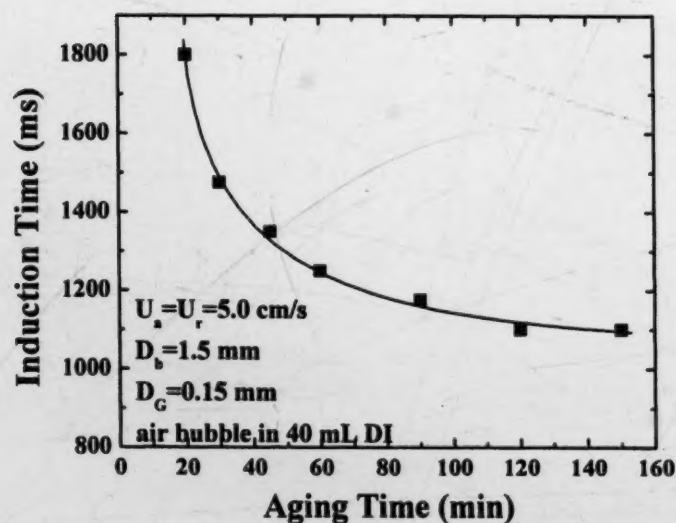


Figure 4-4 Effect of bitumen aging on induction time for air bubble attaching to bitumen in deionized water

that the observed evolution of interfacial tension for the bitumen-aqueous systems by Isaacs and Smolek is similar to that found for aging-dependent induction time shown in Figure 4-4, illustrating a role of interfacial tension in bitumen-bubble attachment. Such aging effects have also been noticed by other researchers (Cayias et al., 1976; Puig et al., 1979). Lack of consistency and reproducibility in interfacial tension measurements for the oil-sulfonate-brine system because of aging phenomena was reported. It was considered that there might be some differences between an unequilibrated and a pre-equilibrated regime for a system containing a highly viscous hydrocarbon phase. Since bitumen/aqueous interfacial phenomenon plays an important role in bitumen-bubble attachment reflected by varying induction time, it is clear that aging effect needs to be carefully considered in induction time measurements. For the purpose of our study, the measurements were carried out two hours after water was made in contact with bitumen to ensure bitumen/water system reaching equilibrium.

4.2.2 Effect of solvent on induction time

Oily collectors are widely used in coal flotation in order to improve coal recovery. Through a suitable hydrocarbon treatment, the hydrophobicity of the coal particles can be altered, selectivity of fine coal flotation is improved, and ultimately the recovery is enhanced (Laskowski, 2001; Peng, 1996; Fan et al., 1989; Laskowski and Yu, 2000). Depending on the quality of the oil, the hydrodynamic conditions, and

the method used to separate the agglomerates, the oil consumption and final result of different processes (agglomeration flotation, emulsion flotation, oil agglomeration, etc.) can be very different. However, in all these processes, it is desired that the second liquid added, oil, must be immiscible with the suspending liquid, and be capable of displacing this liquid from the surface of the treated particles. It has been reported that lighter oils of density below about 0.9g/cm^3 generally give good ash rejection than heavier or viscous oils of complex nature (Leonard et al., 1981). Kerosene is the most commonly used oily collector in fine coal flotation although other oils or hydrocarbons, such as pentane, heptane, diesel, fuel oil No. 2 or Fuel oil No.6, were also used in the production or research work.

To study the effect of solvents on induction time of bitumen-bubble attachment, three different types of oil and solvents (toluene, heptane and kerosene) were used to prepare oily bubbles. The main reasons why we chose these three solvents are (i) they are immiscible with water and can easily cover air bubbles to form oily bubbles; (ii) they can reduce the viscosity of bitumen rapidly after making contact with bitumen; and (iii) kerosene and heptane are commonly used as collectors in coal flotation and have demonstrated their good performance. The results in Figure 4-5 show that the presence of an oily film on air bubbles reduces induction time of bubble-bitumen attachment in deionized water. A reduction in the induction time by 15%, 20% and 50% was observed by using kerosene-, heptane- and toluene-coated air bubbles, respectively. To understand the role of oily film on air bubbles in reducing induction time of bitumen

attachment to air bubbles, we consider three recognized elementary steps, i.e., (1) thinning of the intervening liquid film to a critical thickness; (2) rupture of the intervening liquid film and formation of a three-phase contact nucleus; and (3) expansion of three-phase contact line from the critical radius to form a stable wetting perimeter (Nguyen et al., 1997). It is evident that anything that reduces the time needed for any of these three steps will contribute to the reduction of the measured induction time.

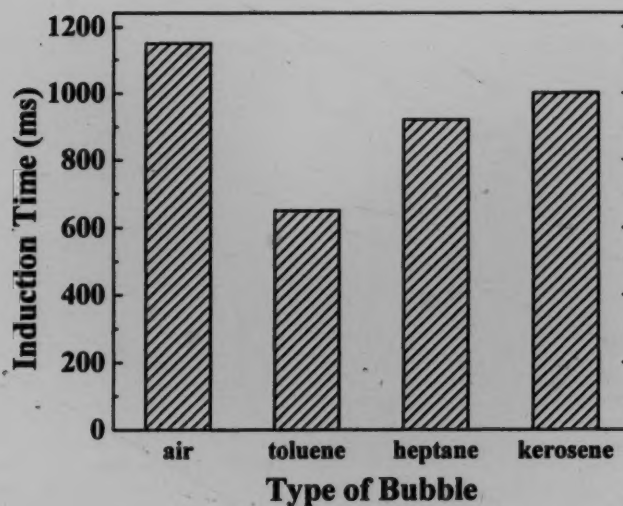


Figure 4-5 Effect of oil or solvent film around air bubbles on induction time of bubble attachment to bitumen in deionized water

When using oily bubbles, the surface properties of air bubbles are changed by the coated thin layer of oil or solvent. As it is known that materials placed on a water surface may spread over to give a monolayer, or may form a lens. Whether or not they can spread on the water surface can be predicted by the so-called spreading coefficient,

which gives the free energy change for the spreading of a film. The spreading coefficient of liquid B over A is given by

$$S_{B/A} = \gamma_A - \gamma_B - \gamma_{A/B} \quad \text{Equation (4-1)}$$

where γ_A , γ_B , and $\gamma_{A/B}$ are the surface tension of material A, B, and interfacial tension between A and B respectively. If $S_{B/A}$ is positive, the spreading of B over A is expected, and it will be accompanied by a decrease in free energy. This typically happens when a liquid of low surface tension is placed on another liquid of higher surface tension. It can be calculated by using Equation 4-1 that the spreading coefficients for toluene, heptane and kerosene on air are 9.27mN/m, 5.2mN/m, and 4.8 mN/m, respectively (Table 4-1). This means that, for these three solvents, whenever the three phases of gas, oil, and water come into contact, the oil phase can form a continuous film between the gas and water. So the oil can spread onto the air bubbles in the aqueous phase to form oily bubbles. It was reported that the velocity of spreading is proportional to the spreading coefficient. The spreading velocity for many polar oils on gas-water interface is about 1-10 cm/s (Davies et al., 1963). In fact, dissolved air flotation is already widely used for oily wastewater cleanup by employing the positive spreading coefficient of oil over air bubbles (Grattoni et al., 2003; Oliveira et al., 1999). During this process, fine air bubbles are created in a water phase containing immiscible oil droplets. After bubble-oil drop contact and rupture of the water film, oil drops have a tendency to spread over the bubbles. Their results showed that the flotation efficiency depends on both hydrodynamic and physicochemical conditions of the system. Spreading coefficient and induction time

were shown to be useful parameters to estimate the efficiency of oily water cleaning by flotation process (Oliveria et al., 1999).

Table 4-1 Pertinent physical properties of the oil and solvents at 20 °C

Oil	Density (g/ml)	Viscosity (mPa s)	Surface Tension (mN/m)	Interfacial Tension (mN/m)	Spreading coefficient of oil on water (mN/m)
Heptane	0.6837	0.409	20.3	47.3	5.2
Kerosene	0.75	0.25	28	40	4.8
Toluene	0.8669	0.59	28.53	35	9.27
Naphtha	0.86	1	19-23	39-51	about 5.2

Air/water interfacial tension is 72.8 mN/m

In a bitumen flotation system, natural surfactants are released from bitumen into the aqueous phase. The released surfactants tend to accumulate at the interfaces as shown in Figure 4-6. Thus, all of the interfaces involved (solid/solution, bitumen/solution, air bubble/solution, and oily bubble/solution) are negatively charged.

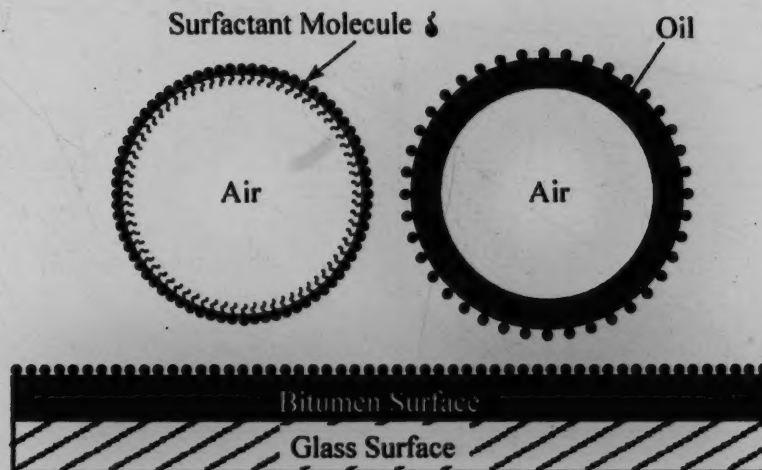


Figure 4-6 Schematic of interfaces of bitumen/water, air bubble/water and oily bubble/water before bitumen-bubble contact

Since interfacial energy for an air-water interface (72mN/m) is much higher than that for an oil/water interface ($35\text{--}47\text{mN/m}$), the released surfactant has higher potency to accumulate at the air/water interface than at the oil/water interface. As a result, the air-water interface tends to be more rigid than oil-water interface. When pressed against bitumen surface, air bubbles exhibit a higher resistance to deformation than oily bubbles, which translates to a stronger resistance to the thinning of intervening water films required for the attachment. On the other hand, when oily bubbles are pressed against bitumen, the surfactant molecules at the interface can retreat into the thin oil layer that covers the bubbles as illustrated in Figure 4-7. This mobility of surfactant molecules allows exposure of fresh oil-water interface near bitumen surfaces, which facilitates film thinning and rupture, consequently, reducing the time needed to establish the attachment. It should be noted that the effect of oil or

solvent film around air bubble on viscosity of bitumen plays a negligible role on film thinning as the contact of oil or solvent with bitumen has not been made during this stage.

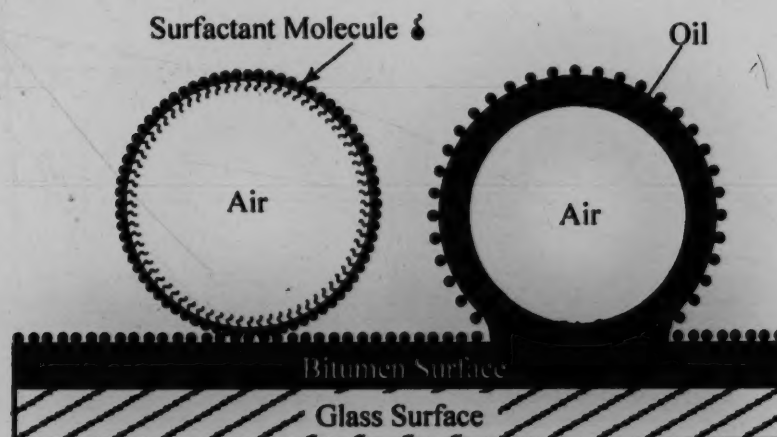


Figure 4-7 Schematic of air bubble/bitumen interface and oily bubble/bitumen interface after bubble/bitumen contact

When a bitumen droplet attaches to an air or oily bubble in a flotation system, the free energy change for the bitumen and droplet is given by the Equation 4-2:

$$\Delta G_{\text{attach}} = \gamma_{a(o)/w} (\cos\theta - 1) \quad (\text{Eq. 4-2})$$

While $\Delta G_{\text{attach}} > 0$ indicates that bitumen-bubble attachment is thermodynamically impossible, the condition $\Delta G_{\text{attach}} < 0$ indicates that it is likely for the bitumen-bubble attachment to take place. An encounter of a bitumen droplet and an air or oily bubble may lead to attachment if their kinetic energy is sufficient to overcome the energy barrier. It is believed that the surfactant transfer from oil-water interface to oil film around air bubble upon compression against bitumen is responsible for reducing the energy barrier for an oily bubble to attach to bitumen surface, which is shown in

Figure 4-8. The reduced energy barrier for oily bubbles will improve the chance of contact and attachment between oily bubbles and bitumen surfaces. Eventually, this is reflected by a shorter induction time for oily bubble/bitumen attachment compared to air bubble/bitumen attachment.

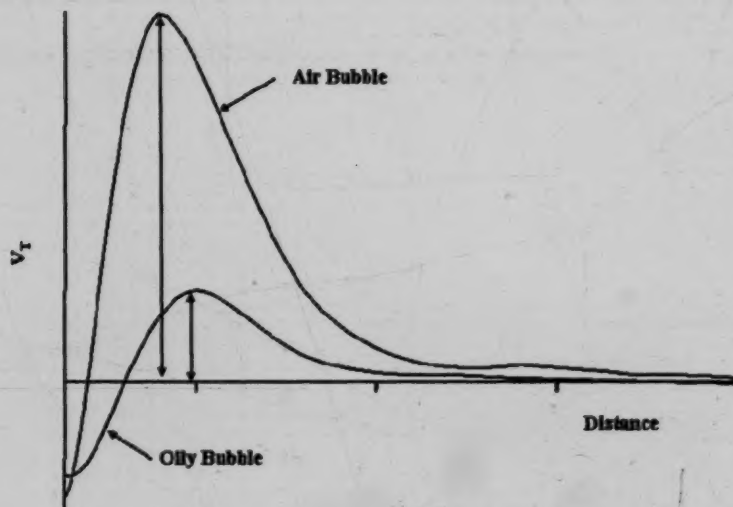


Figure 4-8 Energy diagram of bubble-bitumen attachment

When the intervening water film between the oily bubble and bitumen is displaced and the three phase contact nucleus is formed, the thin oil layer covering the bubble surface will be in contact with the bitumen surface. It is well known that bitumen is highly soluble in some relatively low viscosity solvents such as toluene, naphtha, heptane or kerosene (Table 4-1). The reduction of interfacial viscosity facilitates spreading of three phase contact lines, as shown by the results in Figure 3-4. As a result, the time required for step 3, TPC expansion, mentioned above is reduced.

It appears that the observed reduction in induction time correlates well with increasing solubility of bitumen in these oils. Since bitumen has the highest solubility in toluene, the spreading of toluene-coated bubble should be the highest compared to heptane or kerosene-coated bubbles, reflected by the shortest induction time as measured.

The observed effect of reducing interfacial viscosity by oil or solvent film around air bubbles on bitumen-bubble attachment appears to be related to the general effect of bitumen viscosity on bitumen recovery (Hupka et al., 1983; Schramm et al., 2003). In batch extraction tests, the primary oil recovery and the level of optimal process aid addition were found to be almost unchanged when the operating temperature of the water-based bitumen extraction process was reduced from 80°C to 50°C. However, if the process temperature was reduced further to 25°C, a significant decrease in primary bitumen recovery was obtained (Schramm et al., 2003), which was attributed mainly to high viscosity of bitumen at this low operating temperature. Hupka et al. (1983) reported an excellent correlation between the separation efficiency and bitumen viscosity. Coupled with our results, it is evident that finding a solvent to reduce the viscosity of bitumen and hence to increase bitumen recovery is of increasing interest and importance. Using oily bubble as reported here is an attractive alternative.

4.2.3 Effect of Water Chemistry on Induction Time

4.2.3.1 Air bubbles

The experimental results of contact angle measurement for different bitumen-aqueous systems have shown that contact angle does not respond effectively to the changes of water chemistry (Figure 3-5). To examine whether induction time is a more sensitive marker for bitumen flotation system as reported for other mineral flotation systems, induction time was measured with air bubbles in four different types of water: deionized water and process water from good processing ore, transition ore and poor processing ore, which were also used for contact angle measurement. As shown in Figure 4-9, the induction time value for each type of water increased rapidly with the increase of the size of air bubbles. For the same size of air bubble, a significantly longer time was needed in order for bubble-bitumen attachment to be established in process water compared with the case in deionized water. For example, for a 1.50mm air bubble, the induction time measured in deionized water was only about 800ms. However, induction time value jumped to almost 3000ms in the process water of the good processing ore. While the induction time in the process water from the poor processing ore increased up to more than 6000ms, which almost doubled the time needed in the process water from the good processing ore.

Compared to the results of receding contact angle measurements (Figure 3-5),

induction time shows a much more sensitive response to the changes of water chemistry. Thus, it is shown by the experimental results that the induction time is comparatively a more sensitive marker for bubble-bitumen attachment than contact angle in assessing bitumen flotation. Similar phenomenon was also observed while studying other mineral flotation systems (Yoon and Yordan, 1991; Ye et al., 1989).

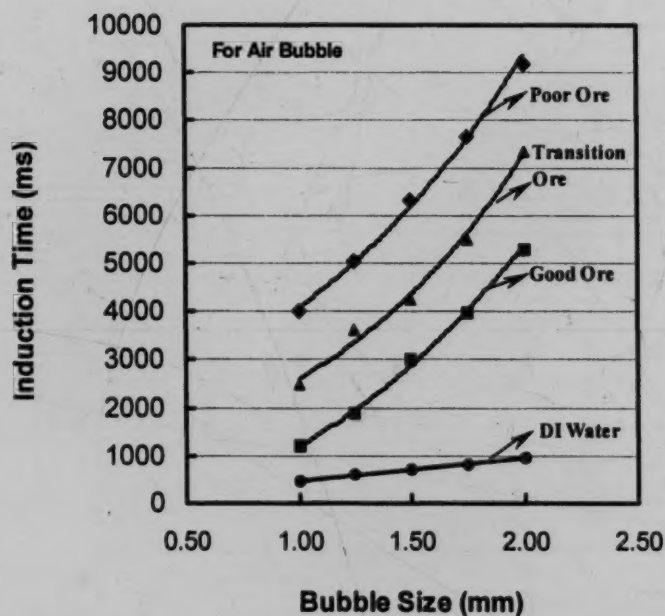


Figure 4-9 Effect of water chemistry on induction time by using air bubbles

4.2.3.2 Kerosene-coated air bubbles

To determine the sensitivity of oily bubble technology to the change of water chemistry in bitumen flotation, induction time between bitumen and air or oily

bubbles is measured in the process water from different grades of ores. Theoretically, any solvent that is immiscible with water and has some solubility for bitumen can be a candidate to generate oily bubbles. Nevertheless, only those that are economically viable, environmentally benign, and operationally safe can be chosen as a solvent in commercial operations. Kerosene-coated bubbles are more viable for commercial applications in oil sands extraction, and preliminary lab experiments have demonstrated that bitumen recovery from poor processing ores could be greatly improved by adding kerosene to the air stream going into the oil sands slurry (Wallwork et al., 2003). Therefore, kerosene-coated bubble was chosen to measure the induction time for this purpose.

As shown in Figure 4-10, the measured induction time becomes less sensitive to water chemistry when kerosene-coated air bubbles were used. In the process water from good processing ores, the measured induction time using air bubbles and kerosene-coated air bubbles is comparative. However, in the process water from the transition ore or poor processing ore, a significant reduction in the measured induction time is observed when oily bubble is used. In fact, the induction time of kerosene-coated air bubbles attaching to bitumen in the process water from transition ores is almost the same as that measured with air bubbles attaching to bitumen in the process water from the good processing ore. This finding clearly indicates that use of oily bubble can mitigate the negative effect of water chemistry on bitumen recovery.

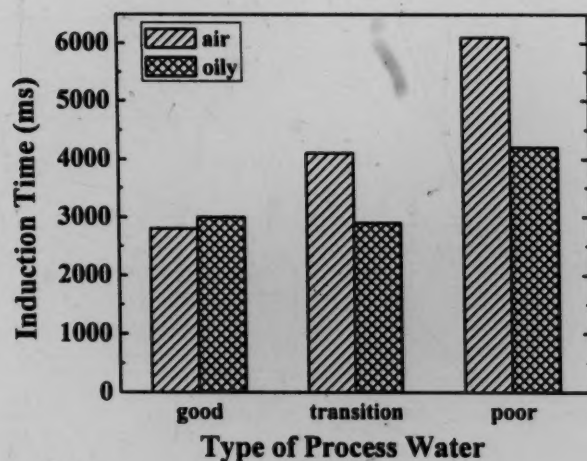


Figure 4-10 Comparison of induction time between air bubble and kerosene-coated air bubbles in process water

4.3 Conclusions

When carrying out induction time measurement for a bitumen-water-bubble system, aging effect should be carefully considered. Other factors, such as the volume fractions and specific interfacial areas, which affect the surfactant partitioning and equilibrium interfacial tension, should also be taken into account in order to obtain reliable and reproducible results of induction time measurements.

Induction time was found to be more sensitive than contact angle to the changes of bitumen flotation system, such as ore grade, water chemistry and surface properties of the bubbles.

Oily films on air bubbles provide flexibility for fine tuning surface properties of air bubbles. The mobility of the bubbles is greatly improved by the coated oil films. The energy barrier to be overcome for air-bitumen attachment to take place is greatly reduced by the coated oil film on the air bubbles. The oil or solvent films around air bubbles can reduce interfacial viscosity at the bitumen-bubble contact area and thus improve the expansion of a three-phase contact line from critical radius to form a stable wetting perimeter.

For different solvents or oils used to generate oily bubbles, the observed reduction in induction time correlates well with the solubility of bitumen in the solvents or oils. In terms of helping reduce the induction time of bitumen-oily bubble attachment, among the three solvents tested, toluene is the best, followed by heptane and kerosene. This order corresponds to the highest bitumen solubility in toluene and the lowest solubility in kerosene.

In the case of poor processing ore or transition ore, the induction time for oily bubble-bitumen attachment is found to be much shorter than that for air bubble-bitumen attachment in the same flotation system of the same solution chemistry.

Induction time becomes less sensitive to water chemistry for kerosene-coated air bubbles, which indicates that the use of oily bubble can mitigate negative effect of

water chemistry on bitumen recovery.

5.0 CORRELATION OF INDUCTION TIME WITH BITUMEN RECOVERY

The experimental results discussed above demonstrated that induction time responds effectively to the changes of ore grade and water chemistry. Compared with contact angle, the induction time is a more sensitive marker to oil sands flotation system. More importantly, the use of oily bubbles could mitigate negative impact of water chemistry on the induction time of air bubbles attaching to bitumen. However, it remains to be established whether the measured induction time can correlate with bitumen recovery in order to use it to evaluate the performance of a bitumen flotation system. To fulfill this task, bitumen recovery data were collected in our laboratory using two distinct flotation devices: a Denver flotation cell and a Laboratory Hydrotransport Extraction System (LHES). Bitumen recovery for three different types of ores, i.e., good processing ore, transition ore and poor processing ore, were collected by using both Denver flotation cell and LHES with air bubble flotation (Figure 5-1). To compare the different performances between air bubbles and kerosene-coated bubbles, LHES was also used to recover bitumen from poor processing ores by flotation as shown in Figure 5-2.

Although the use of different flotation devices resulted in different bitumen recovery due to differences in hydrodynamics, a correlation between induction time and bitumen recovery for each device is evident as shown in Figure 5-1. For bitumen

flotation with air bubbles by Denver flotation cell, the highest bitumen recovery of ca. 95% for good processing ore corresponds to the shortest measured induction time, while the lowest bitumen recovery ca. 75% for poor processing ore corresponds to the longest induction time, with transition ore between the two. It is evident that, for Denver flotation cell, bitumen recovery from oil sands correlates well with the measured induction time, that is, the shorter the induction time, the higher the bitumen recovery. Bitumen flotation by LHES shows a similar correlation although bitumen recovery for each type of oil sand ore is less than the case of using Denver flotation cell which features higher turbulence and aeration rate of the slurry during flotation process because of intense mechanical energy input.

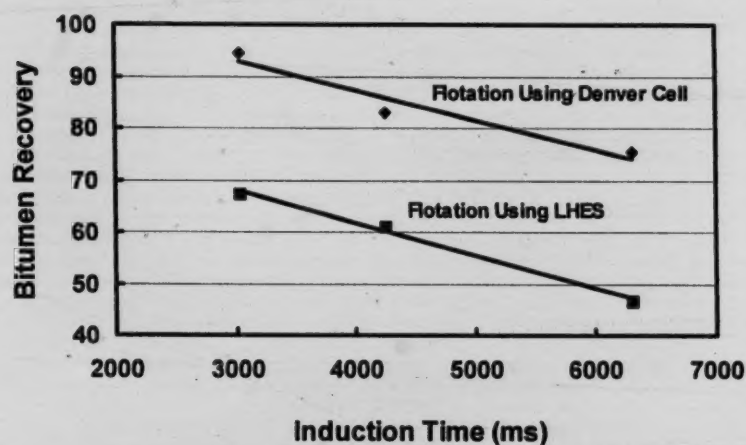


Figure 5-1 Correlations between induction time and bitumen recovery for LHES and Denver flotation cell using air bubble flotation

In flotation tests using a Laboratory Hydrotransport Extraction System (LHES), Wallwork et al. (2003) observed a significant improvement in bitumen

recovery of poor processing ores by using kerosene oily bubbles. The results in Figure 5-2 show that for a typical good processing ore containing 9% of total solids in the

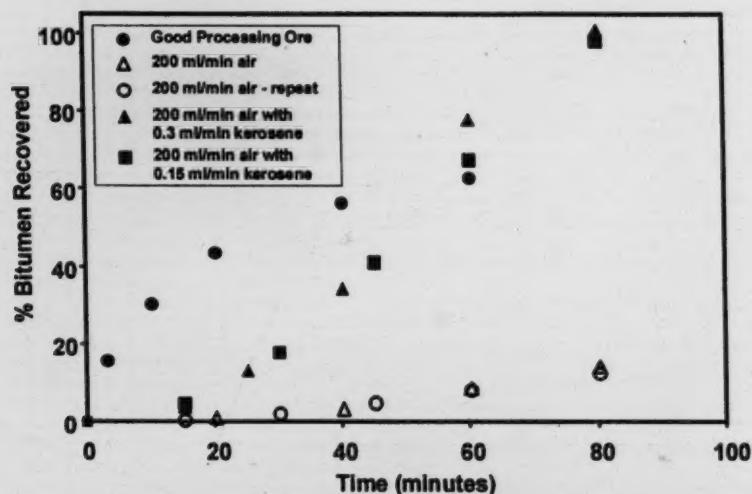


Figure 5-2 Variation of bitumen recovery with time: Effect of kerosene addition to oxidized oil sand ore (reproduced after Vince et al., 2003)

-44 μm size fraction and a bitumen content of approximately 14% by weight, bitumen recovery higher than 95% could be easily accomplished (solid circles), provided that a sufficient flotation time (80 minutes) was allowed. In contrast, bitumen recovery hardly reached 20% when the oxidized ore was processed by air injection (open circles and up-triangles). With the addition of kerosene into the air stream, bitumen recovery from the oxidized ore became comparable or even exceeded that from the good processing ore without kerosene addition (solid up-triangles and squares). It is already known from the previous experimental results that the measured induction times of bitumen attaching to an air bubble and a kerosene-coated bubble in the process water from the poor processing ore are about 6300ms and 4200ms, respectively. The

observed improvement in bitumen recovery from the oxidized ore by oily bubbles appears to correlate well with the improved spreading of three phase contact lines for oily bubbles than for air bubbles, thereby resulting in a shorter induction time of oily bubble attachment to bitumen surfaces. Based on the correlations found between the measured induction time and bitumen recovery using air bubbles, it can be concluded that one of the reasons for the improved bitumen recovery from the poor processing ore by using kerosene-coated bubbles is attributed to the reduction of induction time for the attachment of bitumen to kerosene-coated bubbles.

Another possible mechanism that oily bubbles help enhance bitumen recovery is the increased flotation probability by using oily bubbles. During the study of aerosol-enhanced deinking flotation, gas holdup was found to increase when oil was used, indicating that either bubbles were smaller or rose more slowly (Gomez et al., 2001). Thus, the collision probability, P_c , between bubble and particle is increased. Also, according to Equation 2-8, the probability of attachment P_a will increase with a decrease in bubble rise velocity, U_b , and bubble radius, R_b . Ultimately, the probability of particle flotation and recovery are increased. This is consistent with the experimental result.

If the same is true for oily bubble flotation of bitumen, the reduced induction time, t_i , and smaller rising velocity of bubbles, U_b , will collectively result in an increase in the probability of bitumen-bubble attachment P_a . Also, since oily bubbles

rise more slowly than air bubbles in the oil sand flotation system, the probability for bitumen to collide with bubbles, P_c , will also be improved. Eventually, the probability of bitumen flotation is increased and so is bitumen recovery. The observed correlation justifies the use of induction time measurement rather than time-consuming flotation tests to assess the processability of oil sand ores.

5.1 Conclusions

Oily bubbles help improve bitumen recovery from poor processing ores through increasing spreading of three phase contact lines as reflected by reduced induction time of air bubbles attaching to bitumen surfaces. Also, the use of oily bubbles can increase the bubble-bitumen attachment probability, which would translate to a higher bitumen recovery. A good correlation between induction time of bitumen-bubble attachment and bitumen recovery was observed.

6.0 CONCLUSIONS

From this study, the following conclusions are derived:

1. The type of solvent used in generating oily air bubbles showed a marginal effect on the receding contact angle values, similar to those measured with air bubbles. However, the spreading of oily bubbles on a bitumen surface was found to be much faster than that of air bubbles. The increased spreading dynamics may be due to the greatly reduced bitumen viscosity by oil or solvent at the contact region, resulting in a decreased resistance to the expansion of three phase contact lines. Using solvent-coated air bubbles would be beneficial for improving the rate of bitumen-bubble attachment
2. Contact angle was found to be not sufficiently sensitive to reflect changes of bitumen recovery with changing water chemistry, although it can serve as a good measure of surface wettability for most cases.
3. The induction time for oily bubble-bitumen attachment is found to be much shorter than that for air bubble-bitumen attachment in the process water from poor processing ores. Oil or solvent films on air bubbles provide flexibility for fine tuning surface properties of air bubbles. The reduced energy barrier for oily bubble-bitumen attachment and the increased spreading speed of oily bubble on bitumen surface

contribute to the reduction of induction time needed for establishing oily bubble-bitumen attachment compared with the case of using air bubbles.

4. Aging effect, volume fraction, specific interfacial areas, and physical parameters need to be carefully considered when carrying out induction time measurement for a bitumen-water-bubble system.

5. For different solvents or oils used to generate oily bubbles, the observed reduction in induction time correlates well with the solubility of bitumen in the solvents or oils. In terms of helping reduce the induction time of bitumen-oily bubble attachment, among the three solvents tested, toluene is the best, followed by heptane and kerosene. This order corresponds to the highest bitumen solubility in toluene and the lowest solubility in kerosene.

6. The measured induction time becomes less sensitive to water chemistry for kerosene-coated air bubbles, which may mitigate negative effect of water chemistry on bitumen recovery.

7. Induction time correlates well with the corresponding bitumen recovery in bitumen flotation process. Oily bubbles help improve bitumen recovery from poor processing ores through increasing bitumen flotation probability and reducing induction time of oily bubbles attaching to bitumen surfaces.

8. Induction time was found to be more sensitive than contact angles to the changes of bitumen flotation systems, such as ore grades, water chemistry and surface properties of the bubbles and, therefore, it is a more sensitive marker for assessing processability of oil sands ores.

7.0 RECOMMENDATIONS

1. More experimental data for bitumen flotation by Laboratory Hydrotransport Extraction System (LHES), Denver flotation cell or batch extraction unit (BEU) using oily bubble technologies are needed in order to establish correlations between induction time and bitumen recovery for different laboratory scale flotation devices.
2. Using oily bubble technology in oil sands industry still faces engineering challenges. Methods and equipment used to generate oily bubbles at commercial operation scale remain to be developed.
3. The performance of the present oily bubble generator (Wallwork et al., 2003) can be improved by installing temperature and pressure transmitter and automatic control system. A formal safety operation procedure for oily bubble generator is needed for safety reasons.
4. Induction time measurements may serve as another method to evaluate and screen chemical aids or surfactants to be utilized in improving oil sands extraction processes.
5. The possibility of using oily bubble flotation technology in recovering bitumen from various tailings stream needs further investigation.

6. The kinetics and froth quality from oily bubble flotation instead of air bubble flotation need to be further investigated.

7. Mechanisms of oily bubble induction time reduction require further study.

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APPENDIX A

This appendix contains information on the experimental set-up, which includes the picture of the induction timer, the materials used to build up the induction timer, and information on the induction timer software program.

APPENDIX A.1: Picture of Experimental Set-up for Induction Time Measurement

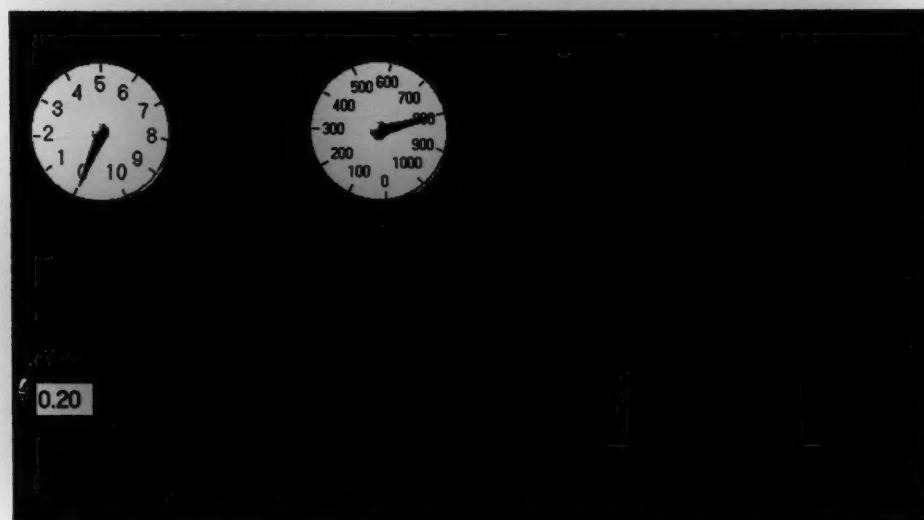


APPENDIX A.2: Induction Timer Material List

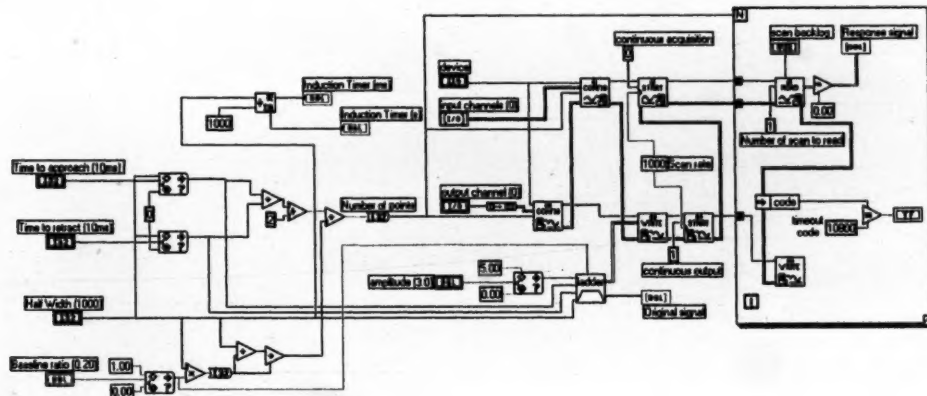
Description	Product Code	Supplier
Data acquisition (DA/AD) board	PC1-6036E	National Instruments
Collector block	777145-01	
Cable	182482-01	
Pulnix ½" format B&W CCD camera	TM-200	Brock Optronics Inc.
Power supply for Pulnix camera	B1.25/12P	
12" B&W monitor	WM-1512A	Brock Optronics Inc.
2 meter video cable to go between monitor and camera	BVCP-2.0-P	
Navitar Precise Eye fine focus body tube	1-61449	Brock Optronics Inc.
Navitar 0.67X adapter for Precise Eye	1-61453	
X-Y-Z positioning stand with 70mm travelX, 60mm travel Y, 65mm travel Z	A03-607	Bock Optronics Inc.
¼-20 adapter plate for monitoring of camera to above	A54-491	
Ulead VideoStudio 6.0 upgrade/ESD	505588	Element
Micro displacement sensor	Z4DF04A	Omron
Breadboard optical stage	07 OBG 502	Melles Griot Canada
5" 2-way speaker	DS55	a&b Sound
ACS Pentium 4 computer system	SYS-WS-P4V1	ASLAN Computer
Tubing, PTFE, 0.052X0.076", 100'	06417-51	Labcor
2mL Syringe	GS-1200	Gilmont Instruments
LabView 6i Software		National Instrument

APPENDIX A.3: Induction Timer Software

APPENDIX A.3.1: Induction Timer Software Control Panel



APPENDIX A.3.2: Induction Timer Software Diagram



Controls and Indicators

[152] Time to approach (10ms)

[132] Half Width (1000)

The total number of scans to acquire from each channel. After acquiring this many scans, the acquisition stops.

[081] amplitude (3.0)

[170] output channel (0)

channels: specifies the set of analog output channels for a group and task. The default is channel 0. You can choose from virtual channels you have previously created by pressing the menu button. See the description of the Analog Output Group Config VI for a detailed description of this parameter and the valid syntax for the channel strings.

[170] input channels (0)

channels: specifies the set of analog input channels for a group and task. You cannot assign a channel to more than one group. The default input is channel 0. You can choose from virtual channels you have previously created by pressing the menu button. See the description of the Analog Input Group Config VI for a detailed description of this parameter and the valid syntax for the channel strings.

[170] channel (0)

channels: specifies the set of analog input channels for a group and task. You

cannot assign a channel to more than one group. The default input is channel 0. You can choose from virtual channels you have previously created by pressing the menu button. See the description of the Analog Input Group Config VI for a detailed description of this parameter and the valid syntax for the channel strings.

(I16) device

(I16) device: the device number you assigned to the plug-in DAQ board during configuration. This parameter defaults to 1.

(I32) Time to retract (10ms)

(DBL) Baseline ratio (0.20)

(U32) scan backlog

(U32) scan backlog: the amount of data acquired minus the amount of data read. If scan backlog increases each time you read data, you are not reading data fast enough for the acquisition. In this case, the new data will overwrite the old data and you will get an overwrite error. Decrease your scan rate, increase the number of scans to read, read the scans more often, or increase the buffer size. See the description of the AI Buffer Read VI for a precise definition of how scan backlog is computed.

(DBL) Response signal

([SGL]) acquired data: displays the data acquired on the specified channels. The transpose option is enabled for this chart so that the data is plotted correctly. Colors have been defined for the first four channels on the chart's legend.

In this VI, the chart's data type is a 2D array. Each row contains one value from each channel for each scan performed by the DAQ board.

(TF) timed out? 2

(TF) TimedOut?: turns on when a trigger does not occur within the time limit in sec parameter.

(DBL) Induction Timer (s)

(DBL) Induction Timer (ms)

(DBL) Original signal